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These proceedings contain the ten presentations made at the workshop by some of the world's foremost experts in the fields of air quality measurement and monitoring. Also included are discussions of the presentations, informal presentations made at the workshop, a concluding discussion of the issues, and the recommendations made by a wrap-up committee formed to review and analyze the workshop proceedings. Among the issues discussed were the differences between four kinetic mechanisms now in existence and between six EKMA field-evaluation methods now available.

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Research Triangle Park, NC
December 15-16, 1981

Edited by

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and
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Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency

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PREFACE

The Empirical Kinetic Modeling Approach (EKMA) is the most recent and presumably the most advanced air quality guideline issued by the U.S. Environmental Protection Agency for use in preparing State Implementation Plans. However, researchers who have used EKMA over the past few years have pointed out two important weaknesses in the approach.

The approach's first weakness is the uncertainty of whether or not the chemical mechanism used in EKMA is the most sound one; several mechanisms are available that could be used. The other major problem with the approach is that it has not been verified adequately. Particularly, results obtained from the approach have not been compared to real atmospheric data. Several methods for the verification of EKMA are also available.

The objective of this workshop was to discuss and rate the methods available for verifying EKMA. The conclusions resulting from the workshop should aid in the development of comprehensive future research programs to address these problems. These proceedings include the text of presentations made at the workshop, follow-up discussions, and the conclusions and recommendations arrived at by a wrap-up committee consisting of Drs. Alan Eschenroeder, Alan Lloyd, Gregory McRae, and Richard Derwent.

ABSTRACT

The U.S. Environmental Protection Agency currently expects to continue recommending use of the Empirical Kinetic Modeling Approach (EKMA) for the preparation of State Implementation Plans aimed at achieving the National Ambient Air Quality Standard for ozone. In view of this fact, efforts to evaluate and document the performance of EKMA as an ozone-predictive model must be continued. To best guide these future efforts, the workshop documented in these proceedings was organized.

These proceedings contain the ten presentations made at the workshop by some by some of the world's foremost experts in the fields of air quality measurement and monitoring. Also included are discussions of the presentations, informal presentations made at the workshop, a concluding discussion of the issues, and the recommendations made by a wrap-up committee formed to review and analyze the workshop proceedings. Among the issues discussed were the differences between four kinetic mechanisms now in existence and between six EKMA field-evaluation methods now available.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AQSM -- Air Quality Simulation Model
BOM -- Bureau of Mines
CDT -- Central Daylight Time
CIT -- California Institute of Technology
CRC -- Coordinating Research Council
EKMA -- Empirical Kinetic Modeling Approach
ERT -- Environmental Research and Technology, Inc.
FID -- flame ionization detector
GC -- gas chromatograhy
HAOS -- Houston Area Oxidant Study
HPLC -- high-performance liquid chromatography
LARPP -- Los Angeles Reactive Pollutant Program
HSD -- Hecht, Seinfeld, and Dodge mechanism
LDT -- Local daylight time
LIRAQ -- Livermore Regional Air Quality model
LST -- Local Standard Time
LT -- local time
MS -- mass spectrometry
NAAQS -- National Ambient Air Quality Standard
NTIS -- National Technical Information Service
OAQPS -- Office of Air Quality Planning and Standards
OZIPP -- Ozone Isopleth Plotting Package
RAMS -- Regional Air Monitoring Stations
RAPS -- Regional Air Pollution Study
RH -- relative humidity
SAI -- Systems Applications, Inc.
SCAQMD -- South Coast Air Quality Management District
SIP -- State Implementation Plan
TACB -- Texas Air Control Board
UASN -- Upper Air Sounding Network
UNC -- University of North Carolina
USC -- University of Southern California
UV -- ultraviolet

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AQSM -- Air Quality Simulation Model
BOM -- Bureau of Mines
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CIT -- California Institute of Technology
CRC -- Coordinating Research Council
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ERT -- Environmental Research and Technology, Inc.
FID -- flame ionization detector
GC -- gas chromatograhy
HAOS -- Houston Area Oxidant Study
HPLC -- high-performance liquid chromatography
LARPP -- Los Angeles Reactive Pollutant Program
HSD -- Hecht, Seinfeld, and Dodge mechanism
LDT -- Local daylight time
LIRAQ -- Livermore Regional Air Quality model
LST -- Local Standard Time
LT -- local time
MS -- mass spectrometry
NAAQS -- National Ambient Air Quality Standard
NTIS -- National Technical Information Service
OAQPS -- Office of Air Quality Planning and Standards
OZIPP -- Ozone Isopleth Plotting Package
RAMS -- Regional Air Monitoring Stations
RAPS -- Regional Air Pollution Study
RH -- relative humidity
SAI -- Systems Applications, Inc.
SCAQMD -- South Coast Air Quality Management District
SIP -- State Implementation Plan
TACB -- Texas Air Control Board
UASN -- Upper Air Sounding Network
UNC -- University of North Carolina
USC -- University of Southern California
UV -- ultraviolet

SYMBOLS

CO -- carbon monoxide
CH_4 -- methane
DNPH -- 2,4-dinitrophenylhydrazine
HC -- hydrocarbon
H_2O_2 -- hydrogen peroxide
HNO_3 -- nitric acid
HO_2 -- hydroxy radical
HONO -- nitrous acid
MBTH -- 2-benzothiazolone hydrazone hydrochloride
NMHC -- nonmethane hydrocarbon
NH_4 -- ammonia
NH_4NO_3 -- ammonium nitrate
NMOC -- nonmethane organic compounds
NMVOC -- nonmethane volatile organic compounds
NO -- nitric oxide
NO_2 -- nitrogen dioxide
NO_x -- oxides of nitrogen
O_3 -- ozone
OH -- hydroxyl
PAN -- peroxyacetylnitrate
RHC -- reactive hydrocarbon
RO_2 -- peroxy radical
SO_2 -- sulfur dioxide
THC -- total hydrocarbon
TNMHC -- total nonmethane hydrocarbon
VOC -- volatile organic compound

1. TREND ANALYSIS OF HISTORICAL EMISSIONS AND AIR QUALITY DATA

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ABSTRACT

Historical trend data for the Houston and Los Angeles regions are used to check the EKMA isopleth method of relating ozone concentrations to precursor control. Historical trends in the ozone precursors (nonmethane hydrocarbons and oxides of nitrogen) are estimated from detailed studies of emissions and ambient data; these precursor trends are entered into the Empirical Kinetic Modeling Approach (EKMA) method to predict historical ozone trends, which are then compared to actual ozone trends to test the EKMA method. The investigation also includes studies of the errors in the historical data bases as well as sensitivity analyses regarding EKMA simulation conditions and precursor ratios. The historical trend analyses are useful not only as a means to validate EKMA, but also as a means to understand the air quality effects produced by source growth and source control in Houston and Los Angeles.

The Houston studies were conducted on a yearly basis from 1974 to 1978 for two ozone monitoring sites. Because historical emission changes in Houston were rather small from 1974 to 1978, a definitive test of the EKMA method cannot be performed with Houston data.

The Los Angeles studies were conducted on a tri-yearly basis from 1964 to 1978 for four ozone monitoring sites. The EKMA model performs fairly well in the Los Angeles validation analysis, although there is a general tendency for predicted ozone trends to underestimate decreases in actual ozone trends. This disagreement apparently cannot be accounted for by error in estimated precursor trends, by meteorological fluctuations in actual ozone trends, or by sensitivity to varied EKMA simulation conditions. The reason for the disagreement appears to be error in the choice of a precursor ratio. Further research should be conducted to test the EKMA chemical-kinetic mechanism and to check the equivalency between ambient and EKMA precursor ratios.

INTRODUCTION

The Empirical Kinetic Modeling Approach (EKMA) has recently been proposed as a method for evaluating ozone (O_3) control strategies. Before the EKMA method is accepted as a reliable technique for control strategy analysis, it should be subjected to validation studies. This paper describes validation studies of the EKMA method using historical trend data for the Houston (Davis and Trijonis, 1981) and Los Angeles (Trijonis and Mortimer, 1981) areas. Specifically, historical trends in the O_3 precursors [nonmethane hydrocarbons (NMHC) and oxides of nitrogen (NO_x)] are estimated from emissions and ambient data; these precursor trends are entered into the EKMA method to predict historical O_3 trends, and the predicted O_3 trends are then compared to actual O_3 trends as a test of the EKMA method.

Historical trend analysis may be the most appropriate and useful way of validating the EKMA method because, in historical trend analysis, the method is tested under conditions that are entirely parallel to the intended use of EKMA in evaluating O_3 control strategies. Historical trend analysis also provides a very convenient format for illustrating the sensitivity of the EKMA method to various inputs, such as the NMHC:NO_x ratio and the choice of specific photochemical simulation conditions. The historical trend data, however, are of interest not only with respect to testing EKMA but also of interest in and of themselves. By conducting a detailed analysis of precursor emission trends, we can show how emissions for individual source categories have changed due to controls and source growth, and how total emissions have changed as a net response to trends for individual source categories. By examining trends in ambient precursor data, we can check the emission trend estimates and verify that control programs and source growth have had the anticipated effects. By analyzing historical O_3 trends, we can investigate whether they make sense in light of precursor changes and meteorological fluctuations. Thus, our studies are useful not only as a means to validate EKMA, but also as a means to understand the air quality effects being produced by source growth and control programs in Houston and Los Angeles.

STUDY AREAS

There are two basic reasons why Houston was selected as a study region. First, as evidenced by the Houston Area Oxidant Study (HAOS) sponsored by the Chamber of Commerce and by several Houston programs sponsored by EPA, a great deal of interest currently exists in the Houston O_3 problem. Second, substantial changes in historical precursor emissions are required for an adequate test of the EKMA method; previous investigations (Tannahill, 1976; Radian, 1977) suggested that large reductions in NMHC emissions, on the order of 20 to 35%, have occurred in the Houston area after 1974. As will be explained later, our detailed analyses of emission and ambient trend data indicate that NMHC emissions changed very little in Houston from 1974 to 1978. This unexpected finding not only contradicted the results of the previous investigations cited above but also implied that definitive tests of the EKMA method could not be conducted with Houston data.

The Los Angeles region offered the best opportunity for EKMA validation studies based on historical trend data. Only Los Angeles could provide nearly two decades of high-quality, spatially resolved, long-term trend data for ambient concentrations of O_3, hydrocarbons (HC's), and NO_x. Only Los Angeles could provide independent data sets regarding the NMHC:NO_x ratios from several monitoring programs. Los Angeles was also unique in regard to the excellence of data for emission trend analysis; the Los Angeles area had unusually good information regarding existing emission levels, source growth rates, and source control levels. Furthermore, Los Angeles met the requirement of historical changes in precursor levels: we know that Los Angeles has undergone significant decreases in HC's and increases in NO_x since the middle 1960's (Trijonis et al., 1978; Trijonis, 1980). Los Angeles, of course, was also an intriguing study area because it has a very severe photochemical smog problem and because there is a controversy regarding the recent lack of air quality improvement.

STUDY DESIGN

The Houston studies were restricted to the years from 1974 to 1978 because of constraints imposed by the availability of ambient O_3 data. The year 1974 served as a base year for the analysis, with predictions made for each of the subsequent years. The Los Angeles study covered the time period from 1964 to 1978. To provide more robust data sets for the Los Angeles analysis, 3-year averages (1964-1966, 1967-1969, 1970-1972, 1973-1975, and 1976-1978) of air quality data were used. The years 1964-1966 served as a base period, with predictions made for each of the subsequent 3-year periods.

The EKMA validation studies were conducted for two O_3 monitoring sites in Houston (Mae Drive and Aldine) and four O_3 monitoring sites in Los Angeles (Azusa, downtown Los Angeles, Anaheim, and San Bernardino). For each of the six study sites, four types of data were used:

- Information on the base-year 6 to 9 a.m. ambient $NMHC:NO_x$ ratio for the source area affecting the site.
- Estimates of historical emission trends for the source area affecting the site.
- Ambient precursor trend data for the source area.
- O_3 trend data for the site.

The source areas for each study site were determined by analyzing wind transport patterns (wind roses, pollution roses, wind streamlines, and/or wind trajectories). The base-year 6 to 9 a.m. $NMHC:NO_x$ ratios for Houston sites were estimated from ambient data collected by the Texas Air Control Board (TACB). The base-period 6 to 9 a.m. $NMHC:NO_x$ ratios for the Los Angeles locations were determined by examining ambient data from several monitoring programs of the early 1970's and by extrapolating the results back to the base period (1964-1966) by historical precursor trends. For both Houston and Los Angeles, historical trends in NMHC and NO_x emissions were documented through a new and comprehensive analysis of growth and control schedules for all major source categories. In fact, a sizeable fraction of the entire project resources were devoted just to the emission trend analysis. Ambient precursor trends were examined in detail for both Houston and Los Angeles to verify the emission trend results. The final input to the study, ambient O_3 data, consisted of yearly or tri-yearly O_3 air quality indices (e.g., yearly 1-h O_3 maxima or 95th percentile of daily 1-h O_3 maxima).

The procedure for the study was to locate the base-period point on the EKMA diagram using the base-period NMHC:NO_x ratio and the base-period value of the O_3 air quality index. The historical precursor changes (based on emissions and/or ambient precursor trends) were then used to locate points on the EKMA diagram for subsequent years. The O_3 values predicted by EKMA for the subsequent years were then compared to actual O_3 levels as a test of the EKMA model.

In the analysis, we included error bounds for both the predicted and actual O_3 trends. The error bounds on the predicted O_3 trends represent the uncertainties in our emission trend estimates and the uncertainties in the base-year ambient NMHC:NO_x ratio. The error bounds on the actual O_3 trends represent the statistical variation in the O_3 trend index caused by yearly weather fluctuations. Our studies included special analyses that allowed us to quantify these various sources of error. The error bounds on both the predicted and actual O_3 trends were critical in interpreting the results of the validation tests.

As part of our studies, we also investigated the sensitivity of the results to the specific EKMA simulation conditions. The "standard" EKMA isopleths pertain to the maximum O_3 produced during 10-h irradiations under the following conditions: diurnal sunlight intensity corresponding to 8 a.m. to 6 p.m. LDT for the summer solstice at 34°N latitude; a dilution rate of 3%/h for the first 7 h and zero dilution thereafter; no emissions after 8 a.m.; no transported or advected O_3; and a HC mix of 25% propylene and 75% n-butane with aldehydes of 5% the initial NMHC. In addition to the "standard" EKMA isopleths, we considered isopleths that included emissions after 8 a.m. and special dilution patterns. We also considered isopleths representing O_3 at fixed irradiation times (specific to the individual monitoring site) rather than maximum O_3 over the entire irradiation period.

HOUSTON RESULTS

Historical Precursor Trends

The most difficult and time-consuming task in our Houston study was the compilation of historical emission trends for the O_3 precursors, NMHC and NO_x. We compiled quite detailed emission trend information -- year-by-year emissions from 1974 to 1978 for 26 NMHC source categories and 15 NO_x source categories. For each source category, emission trends are governed by three factors: uncontrolled emission levels, growth of source activity levels, and the timing and effectiveness of controls. Each of these three factors often involves considerable uncertainty. To minimize these uncertainties, we used the most accurate and up-to-date information available from industrial representatives, consulting firms, trade associations, and various local, state, and federal agencies. Despite our efforts, certain information gaps persist which lead to significant uncertainties in the emission trend estimates for Houston.

Figure 1-1 summarizes the total NMHC emissions in our Houston study region (Harris County, Brazoria County, and Galveston County). To simplify this figure, we have summarized the 26 NMHC source categories according to four major source types: the chemical industry, the petroleum industry, motor vehicles, and other sources. Figure 1-1 shows that total emissions in the three-county study region decreased 17% from 1974 to 1976, and increased 12% from 1976 to 1978, so that only a slight NMHC reduction (7%) occurred from 1974 to 1978. The single major source category undergoing a significant reduction in NMHC from 1974 to 1978 was the chemical industry which, despite extremely rapid growth in output, managed to decrease NMHC emissions by 34%. Although some degree of control was installed on all other major NMHC source categories (both stationary and mobile) from 1974 to 1978, these controls were insufficient to overcome growth rates; thus, NMHC emissions from the petroleum industry, motor vehicles, and other sources increased slightly from 1974 to 1978. The two major reasons for the lack of significant NMHC reductions in the Houston region from 1974 to 1978 were rapid source growth (activity increases of 78% for the chemical industry, 24% for the petroleum industry,

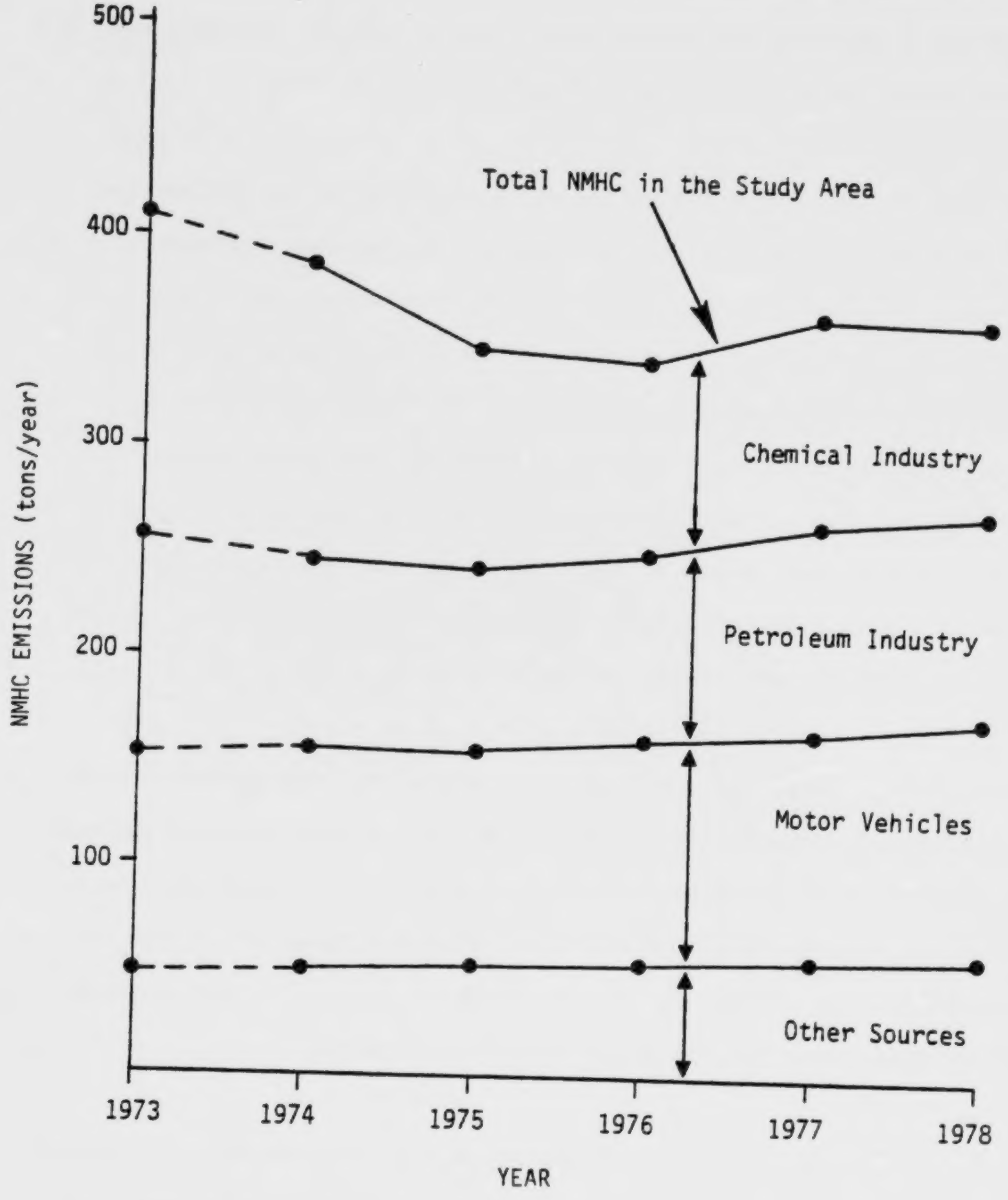


Figure 1-1. NMHC emission trends for the Houston study area.

30% for motor vehicles, and 16% for other sources) and the fact that most of the stationary-source controls were already in place by 1974.

Figure 1-2 shows that the estimated NO_x emissions in the three-county region rose by 18% from 1974 to 1978. The NO_x increase was a product of high growth and the absence of NO_x controls (except for automobiles). The predominant part of the NO_x rise resulted from a 43% increase in chemical industry NO_x over the 4 years. Increases in NO_x from other sources from 1974 to 1978 were as follows: petroleum industry, 13%; power plants, 15%; motor vehicles, 7%; and all other sources, 13%. The increase in NO_x emissions from the chemical and petroleum industries would have been substantially greater were it not for a voluntary fuel conservation program that significantly decreased fuel use per pound of product.

In addition to determining total three-county emission trends, we also estimated emission trends for various subregions. Phenomenological analysis of O_3 and wind data indicated that Harris County should be considered as the basic source area for O_3 at the Mae Drive and Aldine study sites. The net percentage emission changes for Harris County are similar to, but slightly different from, those for the entire three-county region.

To check the emission trend estimates, we also examined ambient precursor trends for 1974 to 1978. The ambient trend analysis was based on regression lines fit to NMHC and NO_x data at Mae Drive and Aldine for three air quality indices: 6 to 9 a.m. concentrations averaged over the smog season,

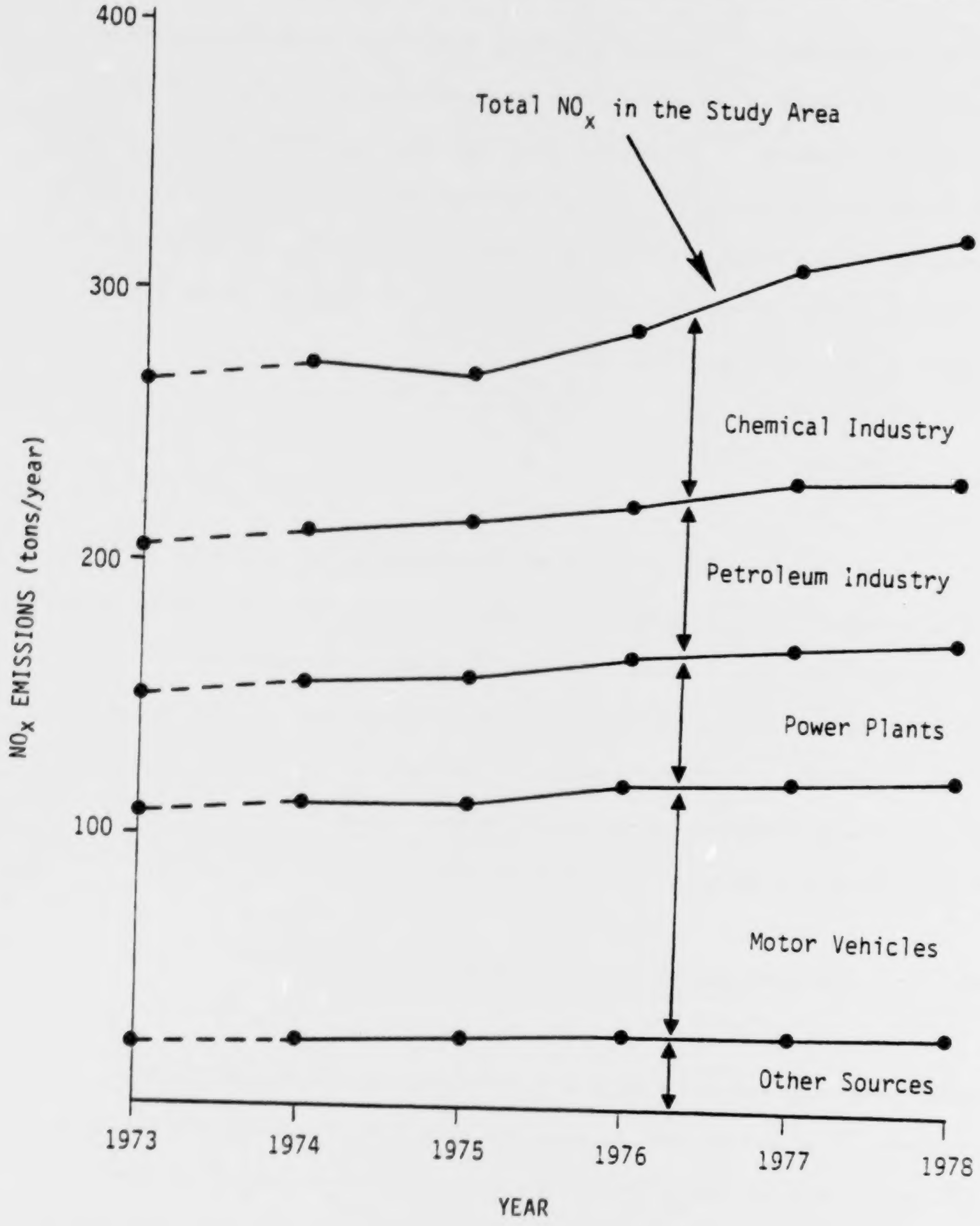


Figure 1-2. NO$_x$ emission trend for the Houston area.

6 to 9 a.m. concentrations averaged annually, and annual mean concentrations (all hours). The ambient data present a more pessimistic picture than our emission trend estimates. The ambient data indicate that NMHC concentrations increased somewhat (on the order of 7 to 23%) and NO_x concentrations increased substantially (on the order of 16 to 48%) from 1974 to 1978. It should be noted, however, that the ambient trend data (like the emission trend data) also involve significant uncertainties.

Historical O_3 Trends

Figure 1-3 illustrates the historical O_3 trends at Mae Drive and Aldine. Two of the three air quality indices included in Figure 1-3 (the yearly second maximum 1-h concentration and 95th percentile of daily 1-h maximum concentration during the smog season) were used in the EKMA validation study. Figure 1-3 shows that no overall trends are evident in the O_3 data from 1974 to 1978. The only exception is the yearly second maximum at Aldine which displays an anomalous decrease from 1975 to 1978.

$NMHC:NO_x$ Ratio and EKMA Simulation Conditions

After examining ambient 6 to 9 a.m. $NMHC:NO_x$ ratios during the smog season at Mae Drive and Aldine, we conclude that a median base-year ratio of 17:1 is appropriate for use in EKMA. In arriving at this ratio, we have divided the raw data for NMHC by a factor of 0.7 to make the NMHC data (based on methane-calibrated instruments) approximately equivalent to data based on

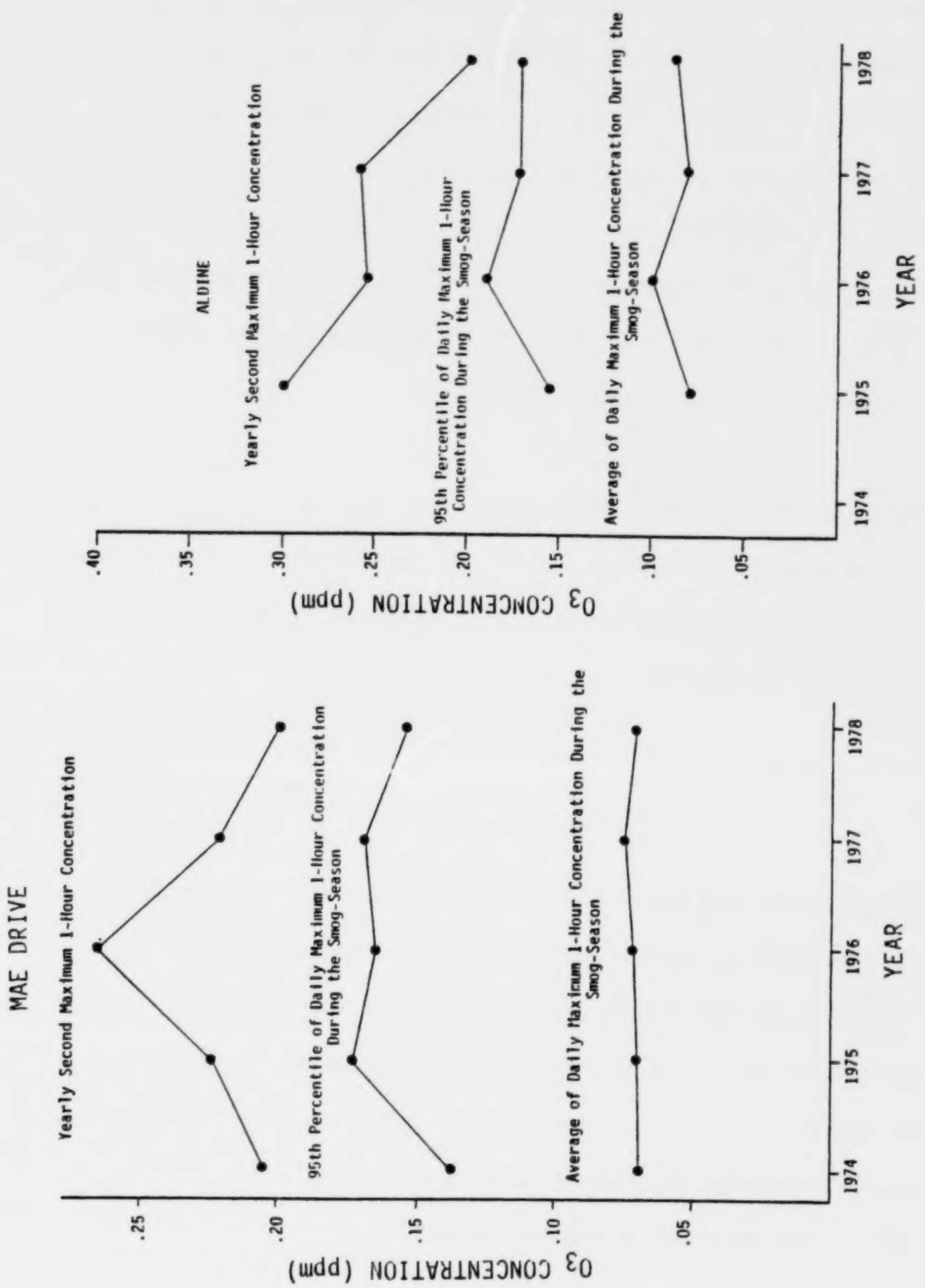


Figure 1-3. Historical O_3 trends at Mae Drive and Aldine.

propane-calibrated instruments (which were used in the chamber studies that serve as a foundation for EKMA). To represent the uncertainty in the ambient 6 to 9 a.m. NMHC:NO_x ratio, we have chosen a low value of 8.5:1 and a high value of 47:1, which are the 10th and 90th percentiles of the ambient values. We find, however, that because of the relatively small emission changes and because of the qualitatively similar variations of NMHC and NO_x emissions from 1975 to 1978, the predicted O_3 trends in Houston are very insensitive to the initial NMHC:NO_x ratio. Uncertainty in the ratio is, therefore, a minor source of error in the Houston validation studies.

Standard EKMA isopleths for basinwide maximum O_3 are used in the validation study. Sensitivity analyses show that, for our particular Houston emission changes, the results of our study are insensitive to the choice of specific EKMA simulation conditions.

EKMA Validation

The Houston validation studies were conducted from 1974 to 1978 at Mae Drive and from 1975 to 1978 at Aldine using two O_3 air quality indices: the 95th percentile of daily maxima during the smog season, and the yearly second maximum hourly concentration. Figure 1-4 presents an example of our results: the tests for the two air quality indices at Mae Drive. As noted previously, the error bars on the predicted O_3 trends represent uncertainties in the NMHC:NO_x ratio and in the emission trend estimates (mostly the latter), and

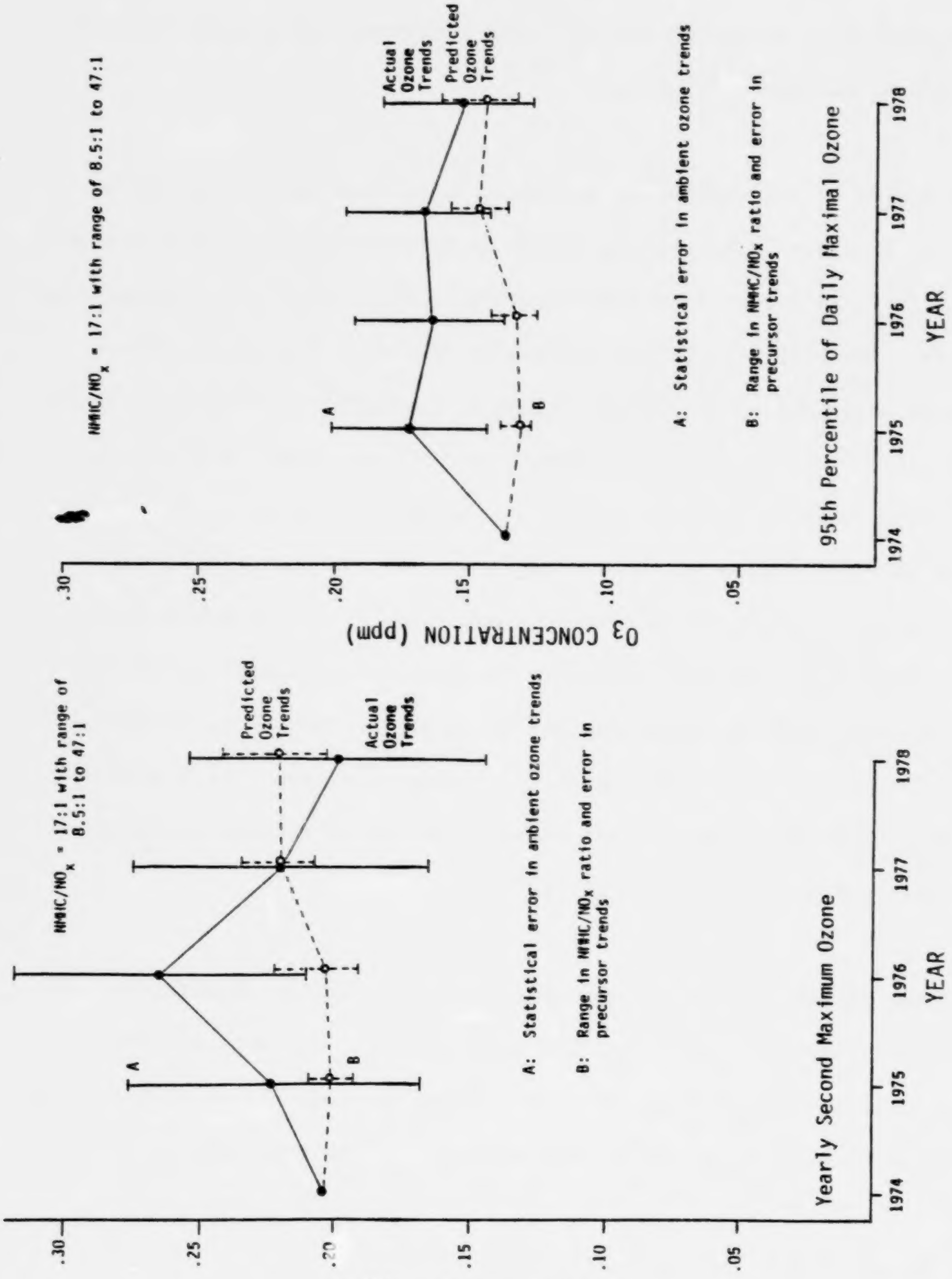


Figure 1-4. Predicted versus actual O_3 trends at Mae Drive.

the larger error bars on the actual O_3 trends represent statistical variance caused by yearly weather fluctuations.

The findings of our validation studies at Mae Drive and Aldine can be summarized as follows: predicted O_3 trends at both sites show little change from 1974 to 1976, a slight increase from 1976 to 1977, and little change from 1977 to 1978. For both air quality indices at Mae Drive and for the 95th percentile of daily maxima at Aldine, actual O_3 trends increase moderately in 1975 and/or 1976 and then decrease somewhat in 1977 and 1978. The net result for these three cases is that the isopleth model underpredicts O_3 somewhat in 1975 and/or 1976 but yields fairly good agreement in 1977 and 1978. The discrepancies could easily be explained by potential errors in the emission trends and, especially, by meteorological variance in the actual O_3 trends. In the fourth case, yearly second maximum O_3 at Aldine, actual O_3 decreased substantially from 1975 to 1978, producing a large discrepancy with predicted trends. This large discrepancy might be explained by an extreme statistical error in this O_3 air quality index at Aldine.

Given the rather large error bounds in our analysis, it is difficult to tell if there is any fault with the EKMA model itself. In fact, a major conclusion of this study is that emission changes in Houston from 1974 to 1978 were not large enough to provide an adequate test of the EKMA model.

LOS ANGELES RESULTS

Historical Precursor Trends

As was the case with the Houston study, much of the effort in the Los Angeles study was devoted to the task of determining historical emission trends for reactive hydrocarbons (RHC's) and NO_x. We compiled the precursor emission trends for Los Angeles year-by-year from 1965 to 1977. Although the Los Angeles emission trends involve significant uncertainties, these are less than those for Houston because better data are available in Los Angeles for base-year emissions, source growth, and control schedules.

Figures 1-5 and 1-6 summarize basinwide emission trends for RHC and NO_x on a yearly basis from 1965 to 1977. As shown in Figure 1-5, estimated basinwide emissions of RHC decreased continually during the study period, with a net reduction of 29% from 1965 to 1977. The predominant part of this reduction was due to decreases in emissions from light-duty vehicles (the largest source category); light-duty vehicle RHC emissions decreased 40% from 1965 to 1977 despite a 54% increase in traffic levels. Organic solvent emissions also underwent a significant (30%) decrease, with this reduction basically occurring between 1965 and 1974.

As shown in Figure 1-6, estimated basinwide NO_x emissions rose rapidly from 1965 to 1973 and then basically leveled off. The net increase over the entire study period, 1965 to 1977, was 34%. The predominant part of this rise

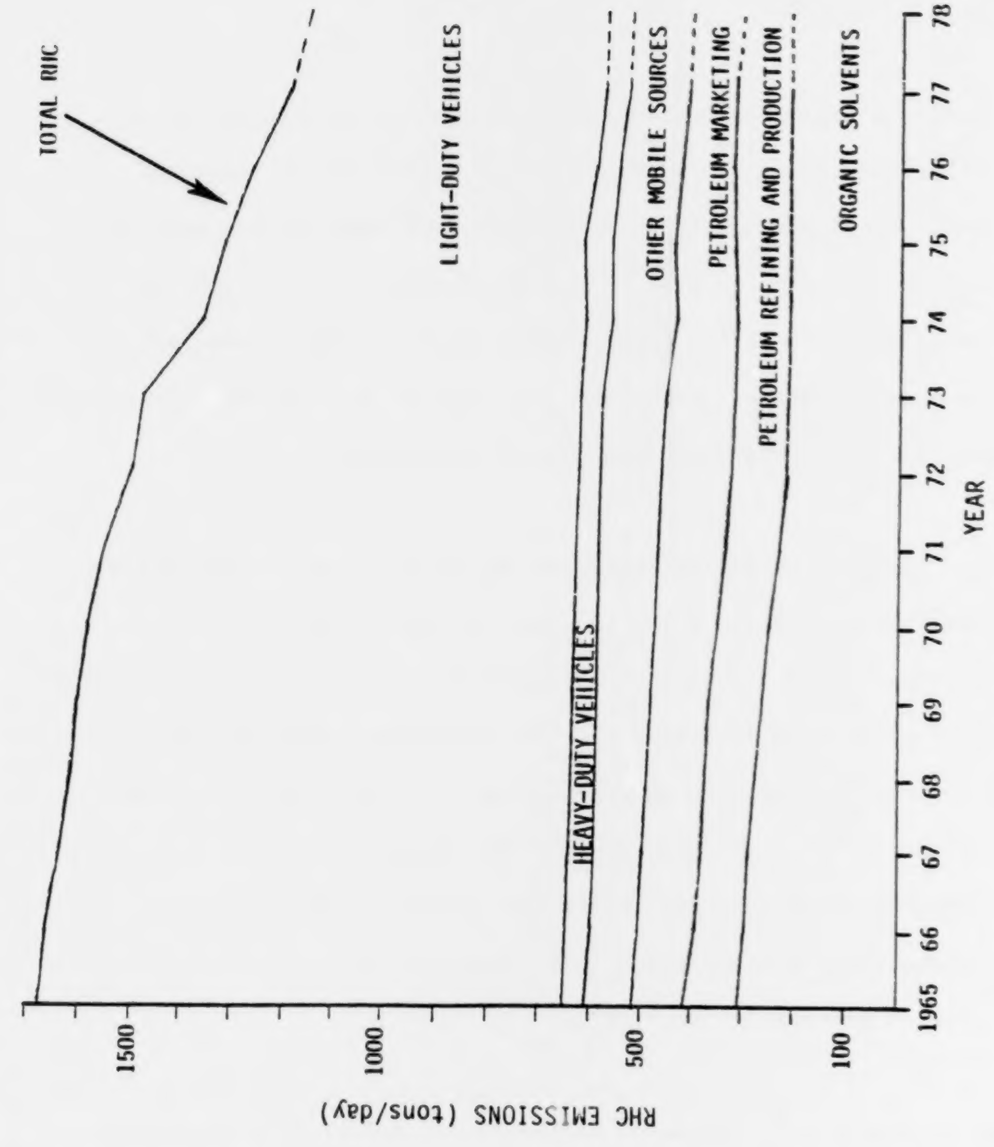


Figure 1-5. Historical RHC emission trends in the Los Angeles basin.

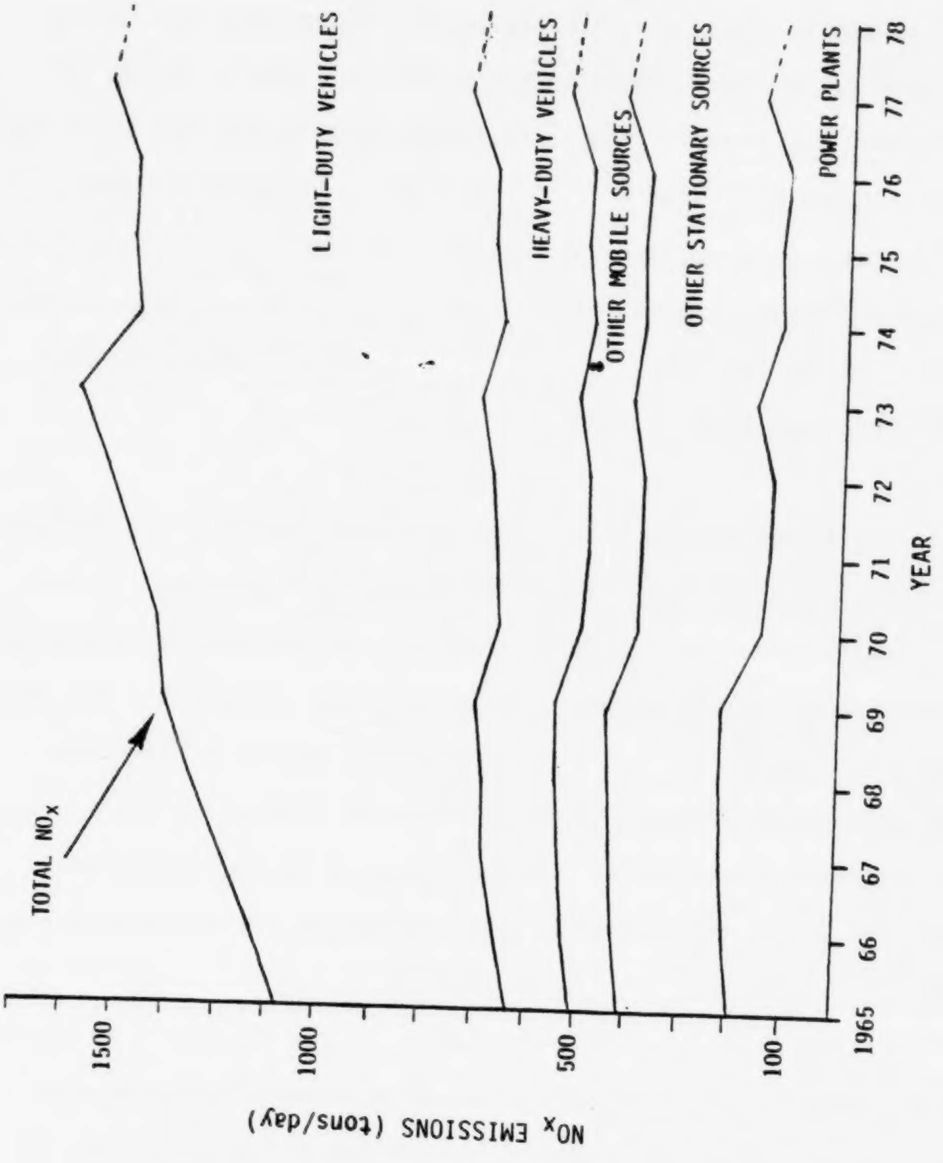


Figure 1-6. Historical NO_x emission trends in the Los Angeles basin.

was due to a 55% increase in NO_x emissions from light-duty vehicles (the largest source category). The net increase in light-duty vehicle NO_x from 1965 to 1977 basically represented traffic growth. Light-duty vehicle NO_x emission factors for new cars jumped upward in the late 1960's, but by 1977 the fleet-averaged NO_x emission factor was reduced back to the 1965 level due to the new car NO_x emission standards of the 1970's. Oxides of nitrogen emissions from heavy-duty vehicles and residential, commercial, and industrial fuel burning also increased significantly from 1965 to 1977, reflecting growth in traffic and natural gas usage, respectively. Power-plant NO_x emissions decreased slightly from 1965 to 1977.

The EKMA validation studies in Los Angeles were conducted using basinwide O_3 trends as well as O_3 trends at four individual monitoring sites: Azusa, downtown Los Angeles, Anaheim, and San Bernardino. In addition to determining basinwide emission trends, we estimated emission trends individually for the source areas affecting the various monitoring sites. Figure 1-7 provides examples of source areas affecting O_3 at downtown Los Angeles and San Bernardino. Emission trends differ somewhat among the various individual source areas, reflecting differences in growth rates and source types within those areas.

Using the numerous long-term monitoring sites in Los Angeles, we also made a detailed study of ambient precursor trends for each source area. As was the case with the emission trend studies, the ambient precursor trend studies included analyses of the errors in the trend estimates.

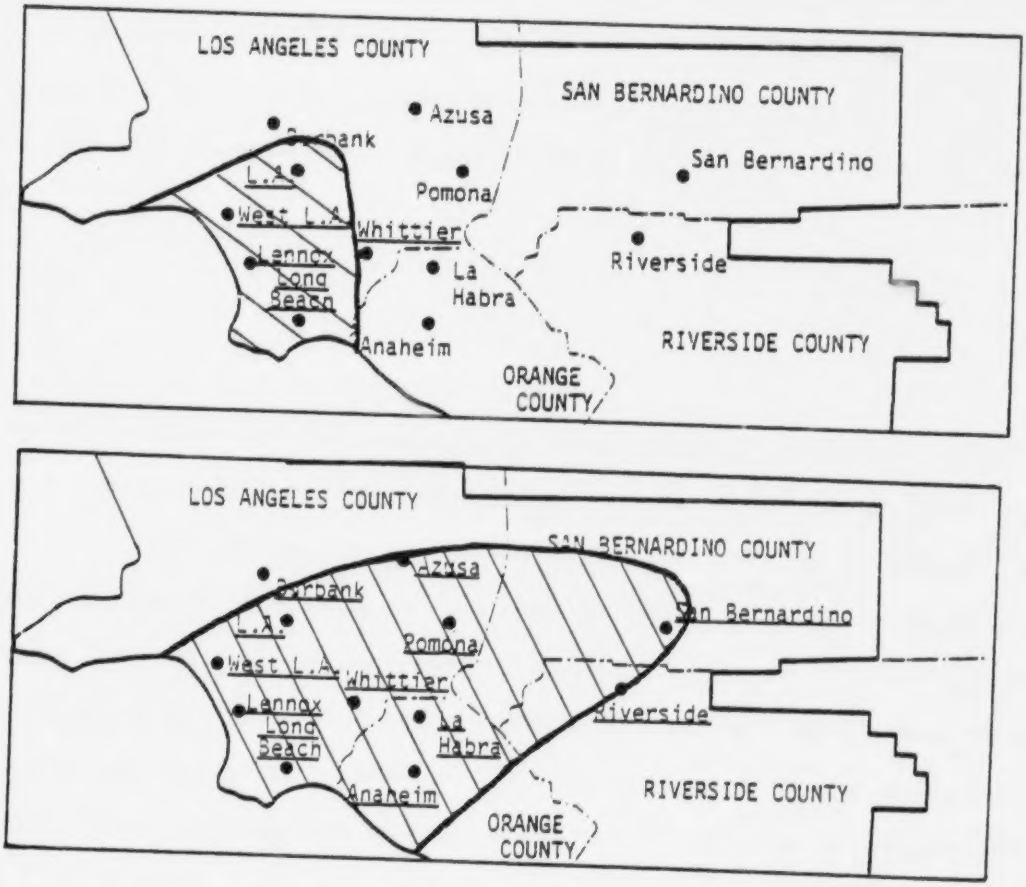

LOS ANGELES COUNTY
SAN BERNARDINO COUNTY
Azusa
Burbank
San Bernardino
L.A.
Pomona
West L.A.
Whittier
Riverside
Lennox
Long Beach
La Habra
Anaheim
RIVERSIDE COUNTY
ORANGE COUNTY
LOS ANGELES COUNTY
SAN BERNARDINO COUNTY
Azusa
Burbank
San Bernardino
L.A.
Pomona
West L.A.
Whittier
Lennox
Riverside
Long Beach
La Habra
Anaheim
RIVERSIDE COUNTY
ORANGE COUNTY

Figure 1-7. Approximate source areas affecting O_3 at downtown Los Angeles and San Bernardino.

Figures 1-8 and 1-9 compare emission trends with ambient trends in various source areas for HC's and NO_x, respectively. As evidenced by these figures, the agreement between emission trends and ambient trends is generally very good, especially when the data are viewed in an overall sense from 1965 to 1977. In light of this agreement, we can state with a high degree of confidence that there has been a moderate (15 to 30%) reduction in HC's and a moderate (25 to 35%) increase in NO_x within the Los Angeles basin from 1965 to 1977.

Historical O_3 Trends

Figure 1-10 illustrates historical O_3 trends at the four study sites for the two air quality indices used in our Los Angeles validation studies: the 95th percentile of daily maximal 1-h O_3 and yearly maximum O_3. The O_3 concentrations at Azusa, downtown Los Angeles, and Anaheim decreased from the middle 1960's to the early- to middle-1970's and then leveled off. All sites in Los Angeles except those in the extreme eastern part of the basin exhibit this historical pattern in O_3 trends (Trijonis, 1980). Characteristic of the far eastern part of the basin, O_3 at San Bernardino increased at a very slight rate during the entire study period.

NMHC:NO_x Ratio and EKMA Simulation Conditions

One of the critical inputs to the EKMA isopleth model is the base-period ambient 6 to 9 a.m. NMHC:NO_x ratio. Our best estimate of this ratio for the

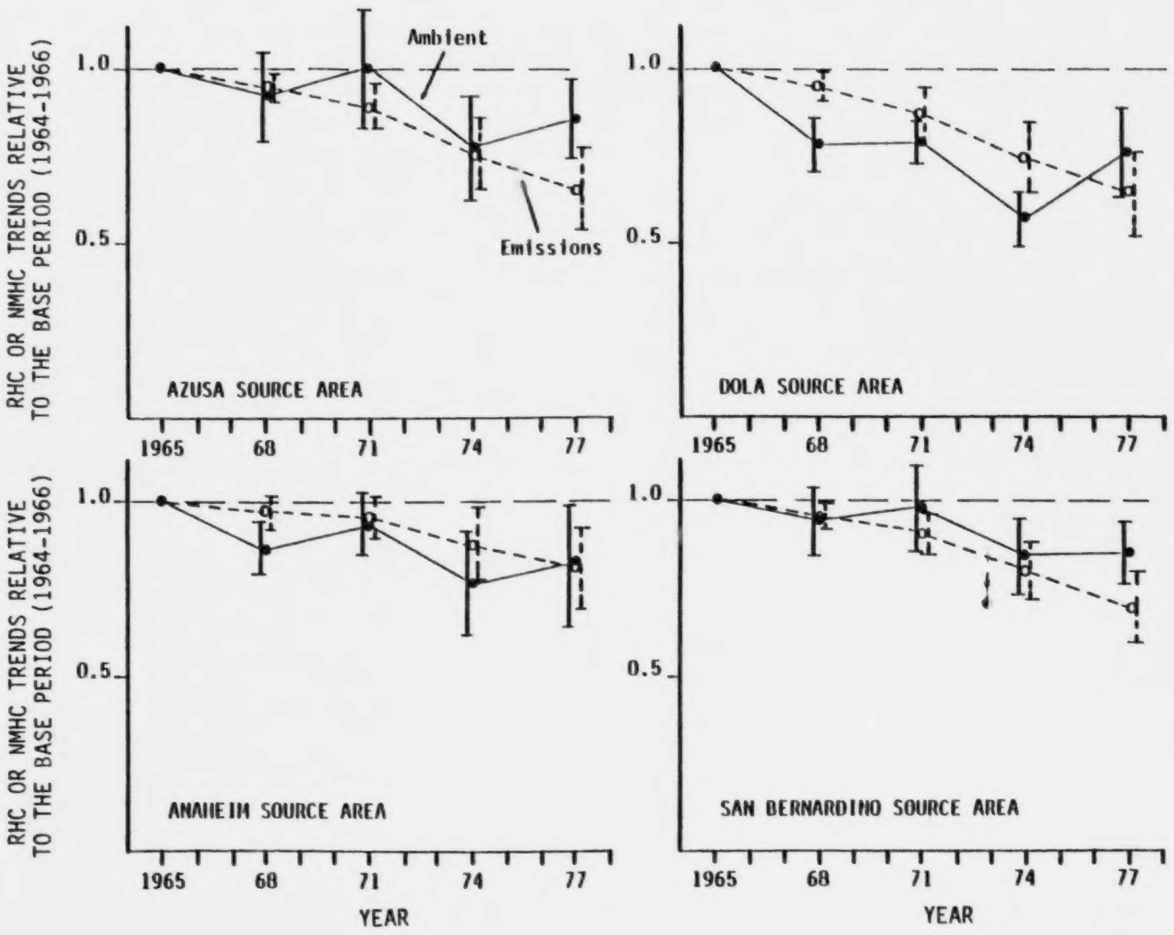


Figure 1-8. Comparison of RHC emission trends (o---o) with ambient NMHC trends (●---●) for various source areas in the Los Angeles region.

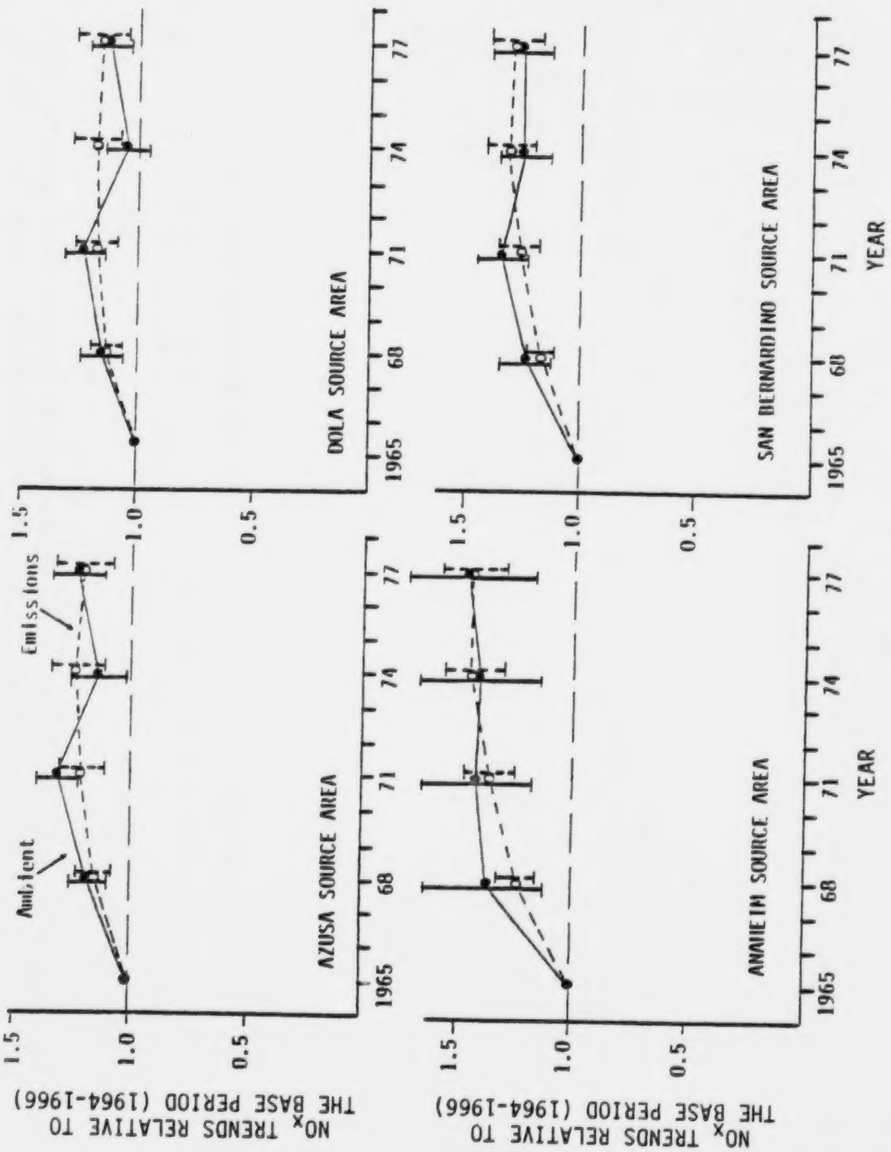


Figure 1-9. Comparison of NO$_x$ emission trends (o---o) with ambient NO$_x$ trends (●—●) for various source areas in the Los Angeles region.

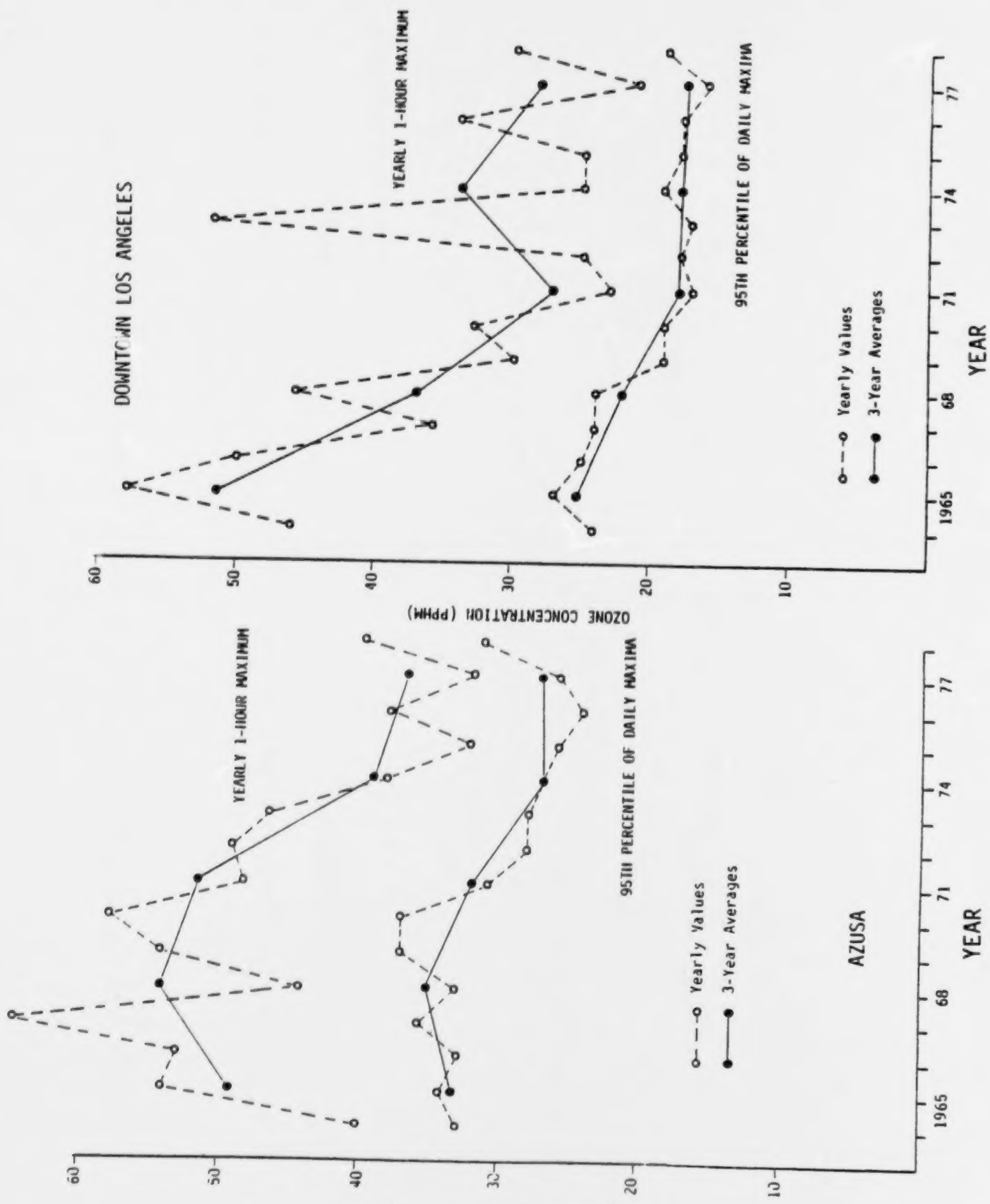


Figure 1-10. Historical O_3 trends at the Los Angeles study sites.

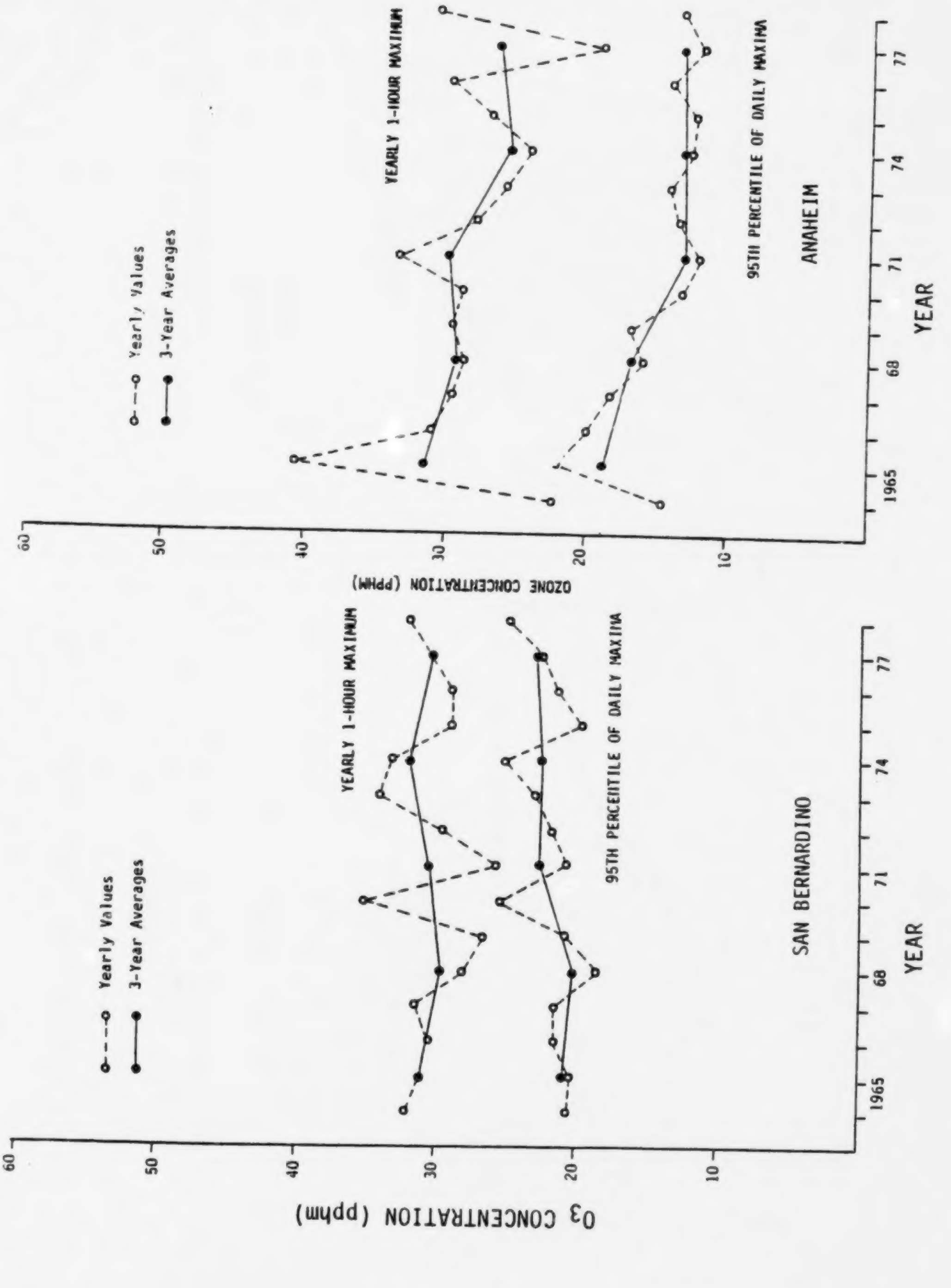
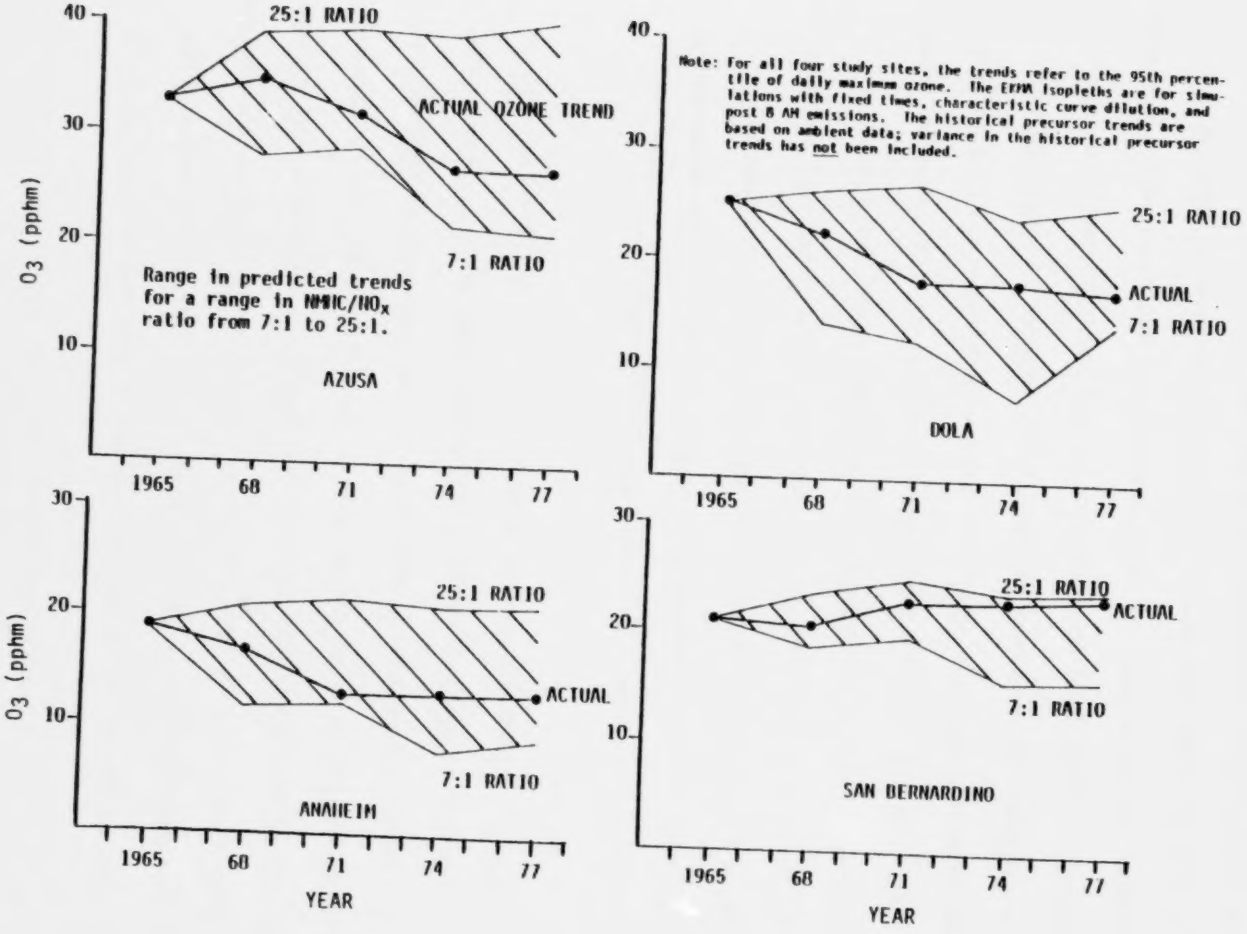


Figure 1-10 (continued). Historical O_3 trends at the Los Angeles study sites.

1964-1966 base period in Los Angeles is 13:1. This estimate is derived by examining data from several monitoring programs during the early 1970's and by extrapolating back to 1964-1966 based on historical trends in ambient precursor levels. In an attempt to make atmospheric NMHC concentrations more nearly equivalent to EKMA NMHC concentrations, the ambient NMHC data are adjusted to correspond to measurements made with propane calibration; the contributions from the nearly nonreactive compounds ethane and propane are also subtracted from the ambient NMHC data. Because of disagreements among various monitoring programs concerning the NMHC:NO_x ratio, because of uncertainties in some of the adjustments applied to the data, and because of stochastic day-to-day fluctuations in the ratio, there is considerable potential for error in our estimate of the NMHC:NO_x ratio. In sensitivity studies, we consider the ratio to range from 7:1 to 25:1.

For the specific EKMA simulation conditions used, and for the type of historical precursor changes examined (decreasing NMHC with increasing NO_x), predicted O_3 trends are extremely sensitive to the base-period NMHC:NO_x ratio. In fact, it is obvious that potential errors in the NMHC:NO_x ratio alone could account for any of the discrepancies between predicted O_3 trends and actual O_3 trends (see Figure 1-11). Holding this conclusion in reserve, we decided to conduct the EKMA validation studies under a very stringent set of test conditions (not allowing for potential errors in the NMHC:NO_x ratio).

The EKMA simulation conditions chosen for this study are the standard conditions except for the inclusion of emissions after 8 a.m. and the use of a



Range in predicted trends for a range in $NMHC/NO_x$ ratio from 7:1 to 25:1.

Note: For all four study sites, the trends refer to the 95th percentile of daily maximum ozone. The EKMA isopleths are for simulations with fixed times, characteristic curve dilution, and post 8 AM emissions. The historical precursor trends are based on ambient data; variance in the historical precursor trends has not been included.

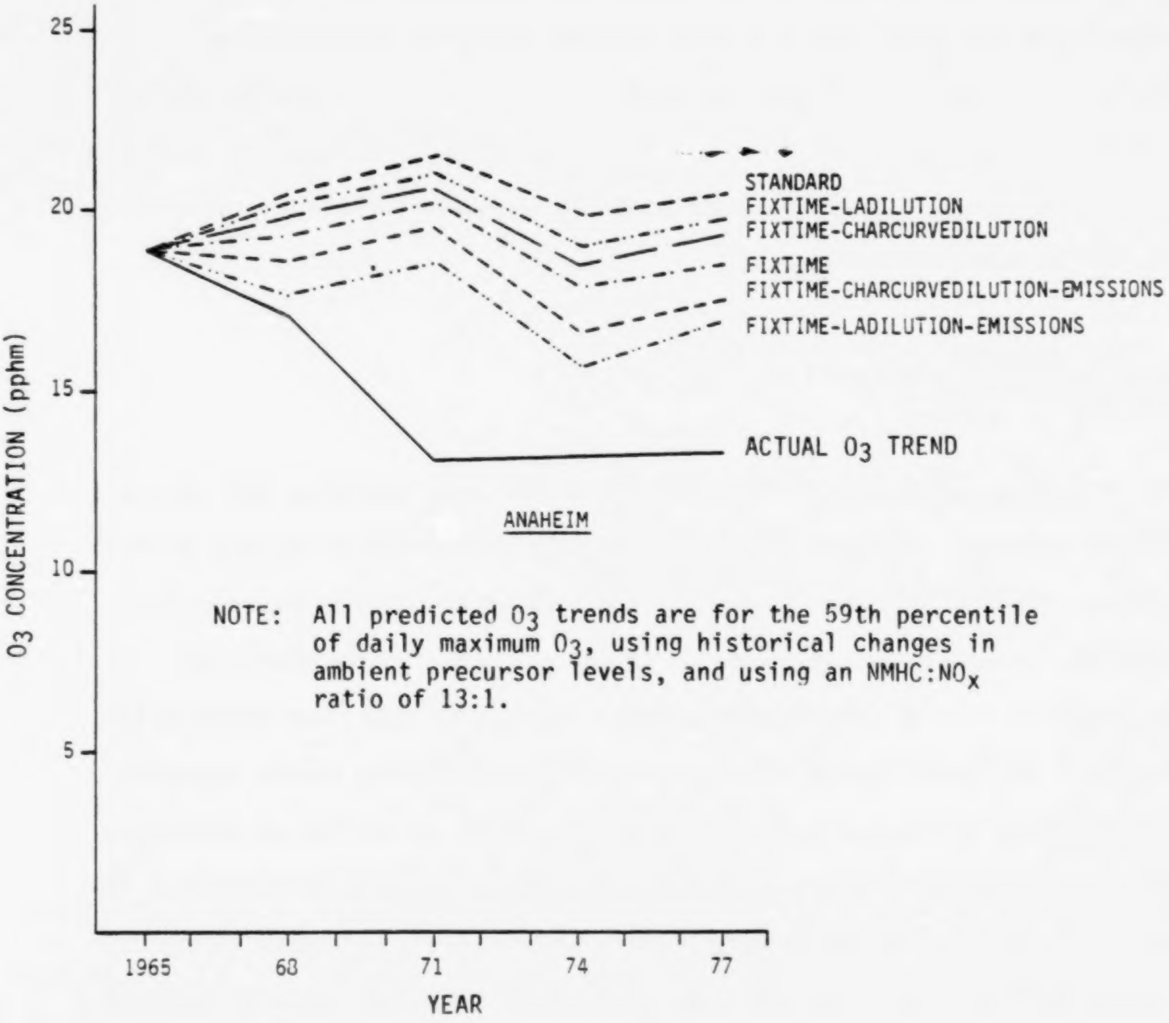
Figure 1-11. Sensitivity of predicted O_3 trends to the range in the $NMHC:NO_x$ ratio at all four study sites.

special Los Angeles-specific dilution pattern. For the studies at individual monitoring sites, we also used isopleths representing O_3 at fixed irradiation times rather than maximum O_3 over the entire irradiation period. A sensitivity analysis using six types of EKMA isopleths indicated that predicted O_3 trends are moderately sensitive to the specific simulation conditions (Figure 1-12). In particular, the addition of emissions after 8:00 a.m. to the model significantly improved the agreement between predicted and actual O_3 trends in Los Angeles.

EKMA Validation

The EKMA validation studies for Los Angeles were conducted for two air quality indices: the 95th percentile of daily maximal O_3 and yearly maximum 1-h O_3. Also, at each site, separate analyses were conducted using either emission trends or ambient precursor trends as inputs to the EKMA model. Figures 1-13 to 1-16 present some example results for Azusa and downtown Los Angeles. In these figures, the error bars on predicted O_3 trends represent uncertainties in the precursor trend estimates; the error bars on the actual O_3 trends represent the meteorological variance in the O_3 trend indices. As noted previously, the Los Angeles results are extremely sensitive to the initial $NMHC:NO_x$ ratio, so that very large error bars would have to be added to represent uncertainty in the $NMHC:NO_x$ ratio.

The results of the Los Angeles EKMA validation studies are nearly the same whether one uses emission trends or ambient precursor trends to derive



NOTE: All predicted O_3 trends are for the 59th percentile of daily maximum O_3, using historical changes in ambient precursor levels, and using an NMHC:NO_x ratio of 13:1.

Figure 1-12. Sensitivity of predicted O_3 trends at Anaheim to various EKMA simulation conditions.

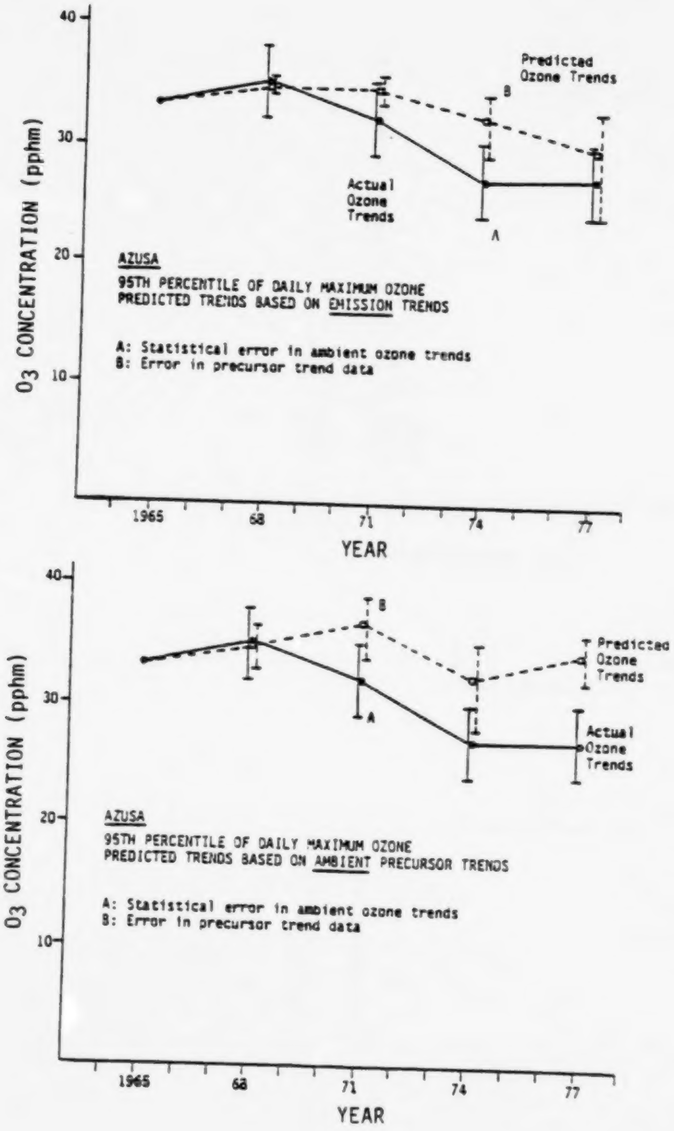


Figure 1-13. Results of the validation studies for the 95th percentile of daily maximum O_3 at Azusa.

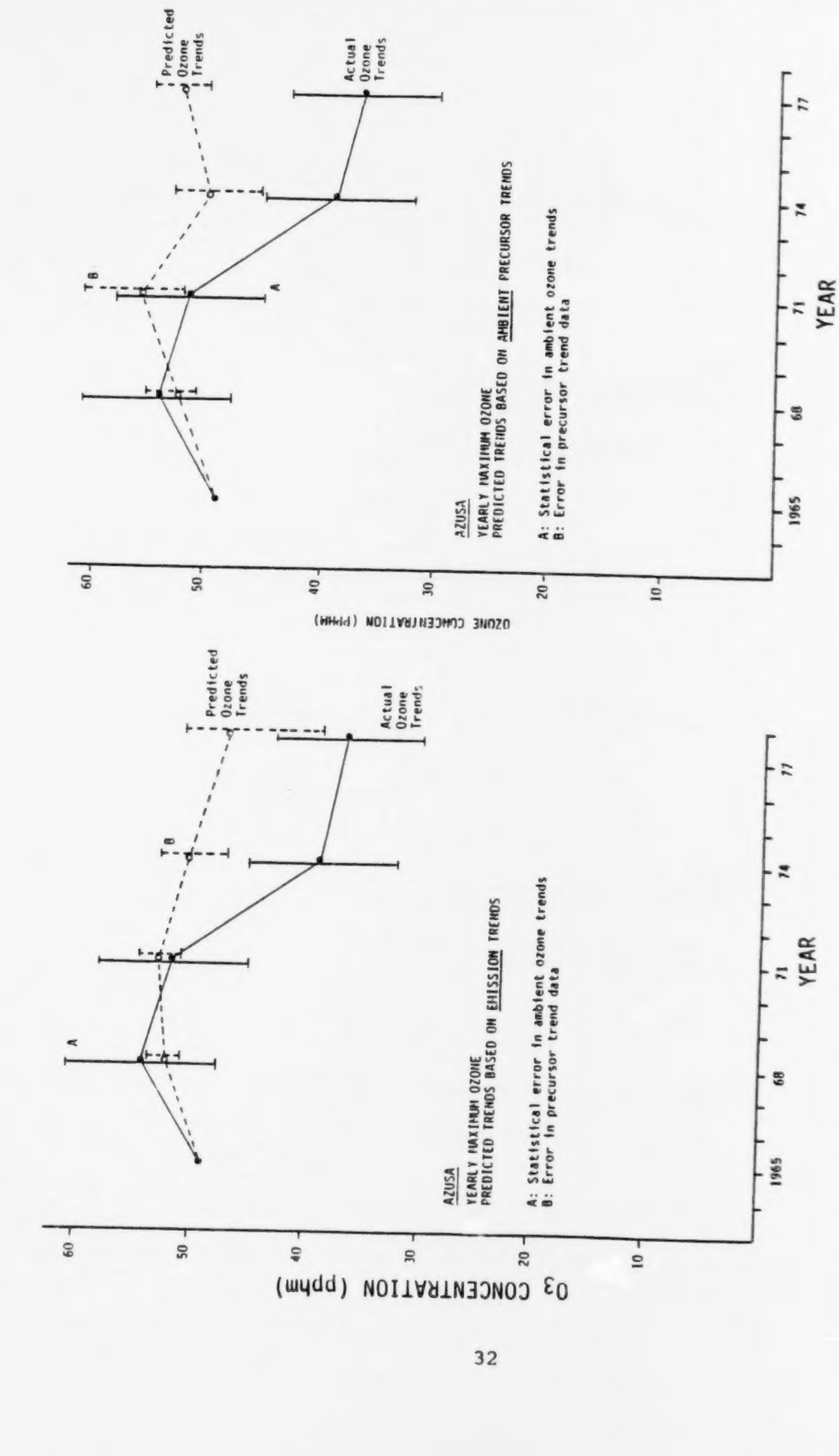


Figure 1-14. Results of the validation studies for yearly maximum O_3 at Azusa.

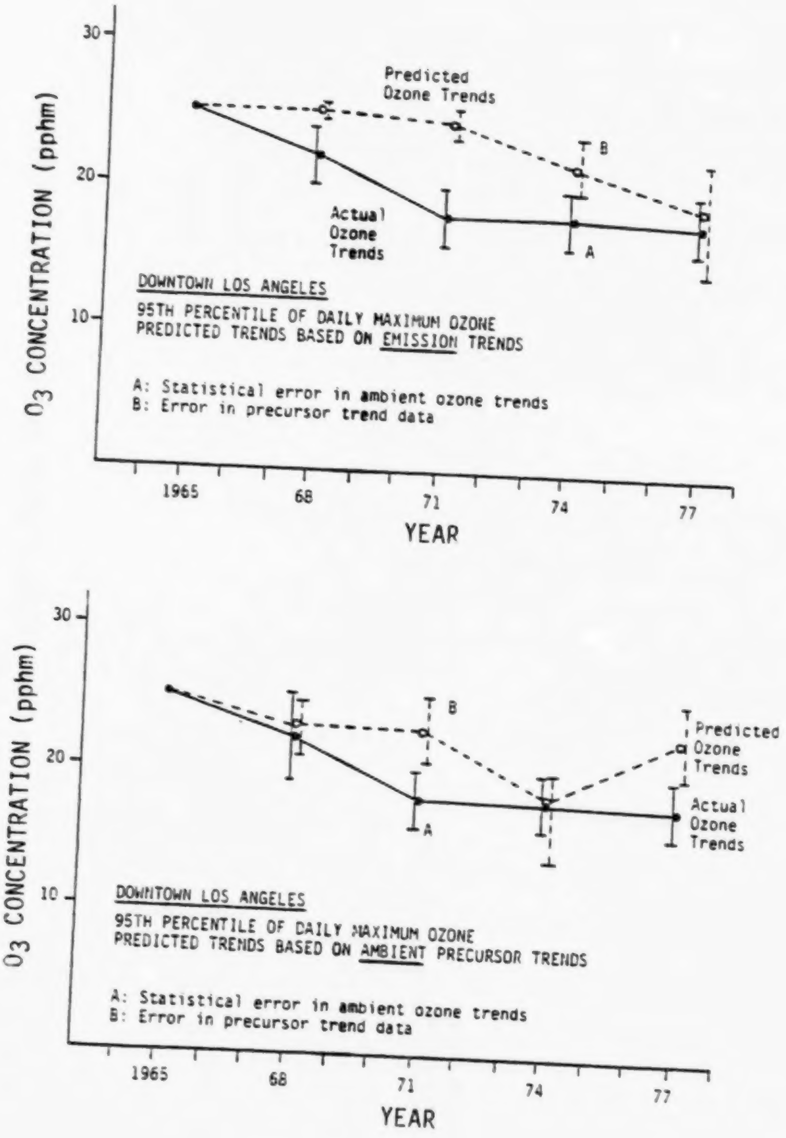


Figure 1-15. Results of the validation studies for the 95th percentile of daily maximum O_3 at downtown Los Angeles.

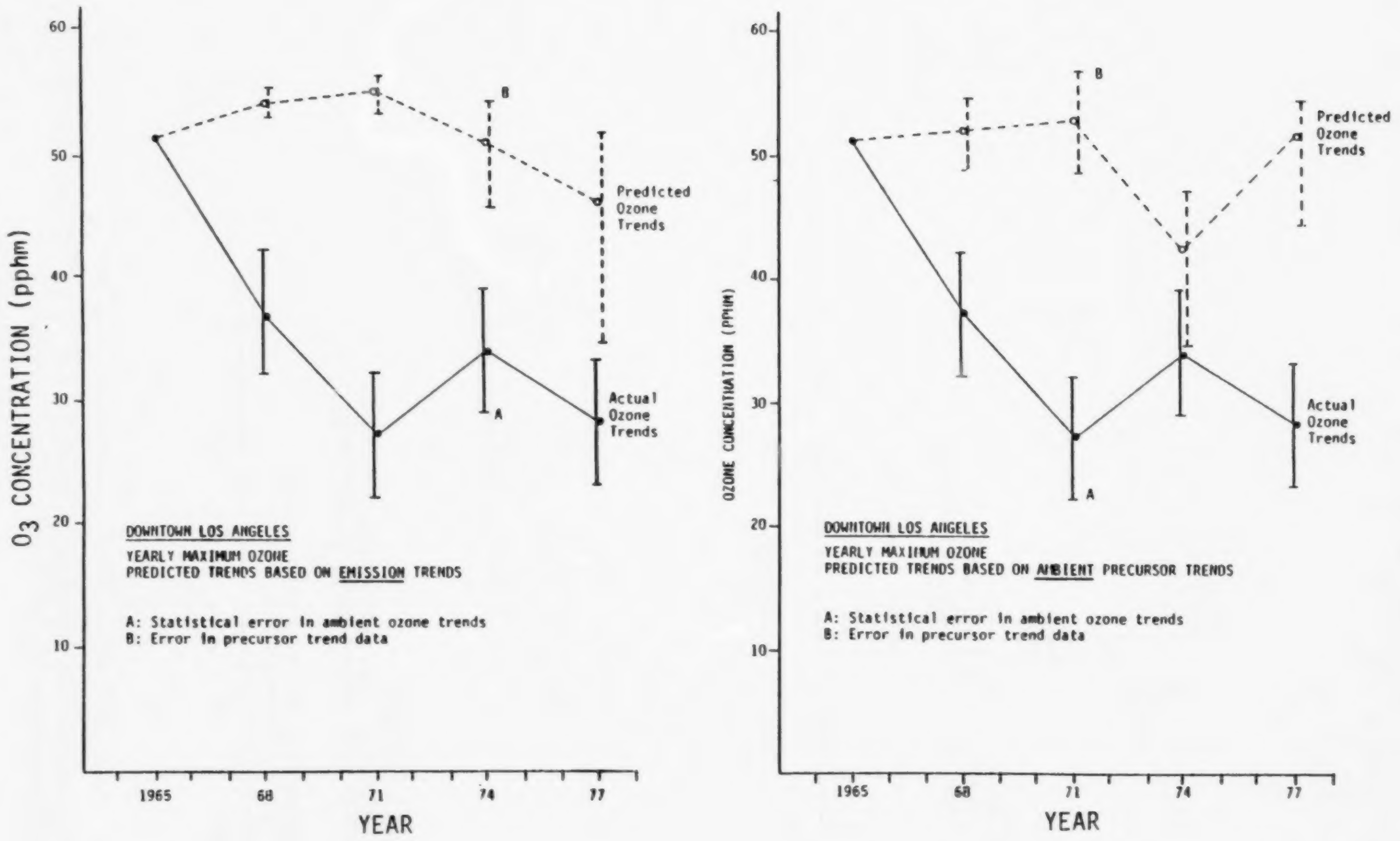


Figure 1-16. Results of the validation studies for yearly maximum O_3 at downtown Los Angeles.

predicted O_3 trends. In both cases, the agreement between predicted and actual trends is not poor considering the stringency of the test conditions (in the sense that potential errors in the NMHC:NO_x ratio are not included). For most sites and years, the predicted and actual O_3 trends agree within the error bars representing variance in precursor trends and meteorological fluctuations in O_3 trends. There is, however, a disturbing general tendency for predicted O_3 trends to underestimate decreases in actual O_3 trends at all sites except San Bernardino. This discrepancy is rather large for certain sites and years.

We are able to eliminate three possible explanations for the general discrepancy that predicted O_3 levels tend to underestimate historical improvements in actual O_3 levels. The cause is not errors in the historical precursor trends, because the error bars on precursor trends are rather small, and because the precursor trends are confirmed by two independent data bases (emissions data and ambient data). Studies of weather-adjusted O_3 data stongly suggest that the discrepancy is also not due to meteorological fluctuations in actual O_3 trends. Also, further refinements in the EKMA simulation conditions (improved dilution patterns, improved estimates of emissions after 8 a.m., addition of carry-over O_3, etc.) will probably not eliminate the discrepancy because our predicted O_3 trends are not quite sensitive enough to changes in the simulation conditions.

The obvious factor that can account for observed discrepancies between predicted and actual O_3 trends in Los Angeles is error in the NMHC:NO_x ratio.

We find that using a 10:1 base-year ratio rather than a 13:1 base-year ratio would eliminate all of the discrepancies. There are two ways in which the NMHC:NO_x ratio could be in error. First, there could be a random error in our estimate of the ratio -- an error that would not necessarily reproduce itself in applying EKMA to other areas. Second, there could be a systematic error in the EKMA chemical-kinetic mechanism or in matching the atmospheric NMHC:NO_x ratio with the EKMA NMHC:NO_x ratio. Further research should be conducted to test the EKMA kinetic mechanism and to check the equivalency between atmospheric and EKMA NMHC:NO_x ratios. This research might lead to improvements in the EKMA chemical mechanism or to guidelines for adjusting atmospheric NMHC:NO_x ratios before they are used in EKMA.

The Los Angeles study points out two potentially significant sensitivities of the EKMA isopleth method. The predictions of EKMA can be moderately sensitive to the specific EKMA simulation conditions and can be very sensitive to the NMHC:NO_x ratio. Thus, it may be important, in some applications, to ensure that the most realistic, area-specific EKMA simulation conditions are used. Also, it may be critical to obtain an accurate estimate of the EKMA-equivalent NMHC:NO_x ratio. Fortunately, predictions of future O_3 trends are likely to be less sensitive to the simulation conditions and to the NMHC:NO_x ratio because future emission changes are likely to involve reductions in both NMHC and NO_x, and because the predictions of EKMA are much less sensitive to the simulation conditions and the NMHC:NO_x ratio when both precursors undergo similar changes.

CONCLUSIONS

Historical trend analysis may be the most appropriate way of validating the EKMA method because, in historical trend analysis, the EKMA method is tested under conditions that are entirely parallel to the intended use of EKMA in evaluating control strategies. Because precursor emissions did not undergo large changes from 1974 to 1978, definitive EKMA validation studies cannot be conducted with the available data for Houston. Historical data for Los Angeles, however, provide a very useful test of the EKMA method.

The EKMA model performs fairly well in the Los Angeles validation studies, although there is a general tendency for predicted O_3 trends to underestimate historical decreases in actual O_3 trends. The reason for this discrepancy appears to be error in the choice of an NMHC:NO_x ratio or error in the sensitivity of the EKMA chemical-kinetic mechanism. Further research should be conducted to test the EKMA chemical-kinetic mechanism and to check the equivalency between ambient and EKMA NMHC:NO_x ratios.

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WORKSHOP COMMENTARY

ESCHENROEDER: What was the data source for your emission inventory; official figures from the district?

TRIJONIS: We compiled a base year from HAOS data or district data, although we also made some of our own calculations for the base-year inventory. To get the source growth rates we went to industry personnel, trade associations, or federal, state, and local agency publications. Then to get the amount of control put on, again we consulted with state and local agencies and industry personnel. We compiled it all ourselves, basically, except for the base-year inventory.

ESCHENROEDER: How were the footprints shown on the map for the source influence areas determined for Los Angeles?

TRIJONIS: Those were determined from a review of various types of wind analyses: wind roses, pollution roses, streamlines, and trajectory analysis. For Los Angeles, we examined previous streamline and trajectory studies. In Houston, we did our own pollution roses, wind roses, and so forth.

ESCHENROEDER: And the sources only in those areas were the ones that you were considering the emission trends?

TRIJONIS: That's correct.

ESCHENROEDER: Finally, were your HC measurements, as far as the ambient measurements or the inventories, in some way corrected to reflect the aldehyde component of organic emissions?

TRIJONIS: No, we didn't consider aldehydes at all. The only ambient and emission HC data we had were for NMHC.

ESCHENROEDER: It's been suggested that that might explain the stronger leverage in the real results than the model would predict. That might be reflected in organic controls and maybe not reflected in the measurements or in the inventories.

TRIJONIS: Yes, that is possible.

McRAE: How sensitive were your results to the choice of the validation statistics? You used two; one was equivalent to the standard, which is the maximum O_3 value exceeded per year; and the other one was the 95th percentile. Error bounds on the 95th percentile seemed to be much better than the use of the statistic corresponding to the standard.

TRIJONIS: In Los Angeles we saw about the same validation results for both the maximal air quality index and the 95th percentile air quality index. Both had a slight disagreement between predicted trend lines and actual O_3 trends. Depending on which sites you looked at, each air quality index had a few error bars that weren't in agreement and a few that were. I don't think the choice was too critical. I'd generally recommend the 95th percentile because it does have a lower variance in the actual trends.

McRAE: The second question I have relates to the use of EKMA. EKMA was basically designed to help the various agencies work out the control requirements to meet the standards. The validation results that you have presented for Los Angeles, for example, are looking at much smaller changes in emissions. Would you care to comment on how you think EKMA might perform when you're talking about changes by factors of two or three in the emissions and relatively small changes in the trends?

TRIJONIS: For Los Angeles, the 29% decrease in RHC emissions coupled with the 35% increase in NO_x emissions was fairly considerable. I wouldn't know about extrapolating that to larger changes. It seems that there is this discrepancy in Los Angeles, and if EKMA were incorrect, I would imagine for larger emission changes the discrepancy would increase. But it is not obvious that there is a problem with EKMA anyway. Our results are very sensitive to the NMHC:NO_x ratio -- future predictions might not be so. Historically, we have been dealing with really rapid decreases in HC's and rapid increases in NO_x. In the future, you would expect that NO_x and HC's would decrease together. In fact, we find that if HC and NO_x emissions are changing in about the same manner, EKMA is very insensitive to the initial NMHC:NO_x ratio. If there is some difficulty matching the ambient and EKMA NMHC:NO_x ratios, it might have been important historically in Los Angeles, but it might not be nearly as important in the future.

LLOYD: Did you examine any data on changes in the chemical composition with time? I realize that the data would be scarce.

TRIJONIS: We examined chemical composition, but not with time. What we did in Los Angeles was take out the ethane and propane in the ambient data to lower our ratio by 10%. I thought of looking at historical changes in composition with time, maybe to track sources with time. We haven't done that, but it would be a very good idea to try to determine the composition trends, especially in Los Angeles. It seems that over the last 3 or 4 years ambient HC's aren't going down while emissions are supposed to be going down. If you looked at trends in the composition you might get an idea of what sources are causing the problem.

McRAE: What about your assumptions for O_3 aloft?

TRIJONIS: We didn't have O_3 aloft built into the model. There is a recent study by Southern California Edison that suggested that once the O_3 goes up the sides of the mountains and goes back over the basin it stays at a fairly high level and very seldom gets re-entrained. We didn't have O_3 aloft in our EKMA simulation conditions.

McKEE: In your graphs from the Los Angeles area, I believe both HC and NO_x emission data showed a sharp break in the curve in 1971. Also, your ambient air monitoring data for O_3 showed a break and a sharp leveling off in 1971. When you compared predicted with actual O_3, you started out with zero difference because that was your base year, and then the discrepancy between actual and predicted values increased to 1971, when it reached a maximum, and then decreased again down to fairly good agreement in the latest years for which comparison was made. My question is, what happened in 1971? Why do all these curves show a sharp break in 1971?

TRIJONIS: There is nothing specific about 1971, although there was an unusual meteorological phenomenon going on. It seems that '69, '70, and '71 were bad years meteorologically for O_3 in Los Angeles, and then '72, '73, and '74, were good years. That might be part of it, but I don't think it is a general phenomenon in all of our validation studies. It might have been true for the two sites and the particular air quality index (95th percentile) I put up there.

There was a break in our emissions data, not in 1971, but in 1974, with the gasoline crisis. Gasoline sales is one of our parameters to track growth, and emissions jogged down especially rapidly for HC's that year, and also for NO_x; 1974 was the only year that NO_x had a significant decrease. So the emissions jump you saw was not in '71 but in '74. And the only thing I can think of special about '71 was that there was a break from 2 or 3 bad years in terms of very high O_3 potential to 2 or 3 good years, meteorologically.

McKEE: Well, it wasn't just '71. I looked at your original report, and there was some sort of a long-term trend for several years which seemed to reach a peak or a nadir or something in 1971, and then that trend reversed over the next several years. So it wasn't just meteorologic emissions in any 1 year.

TRIJONIS: We were grouping the data by 3-year periods. There were a couple of summers in a row during 1972 to 1974 that were good years, i.e., smogless years.

JEFFRIES: What method did you use to generate the isopleth diagrams?

TRIJONIS: One was standard EKMA. Another, instead of isopleths representing maximum O_3 over 10-h radiation, was O_3 exactly at 7 h; another one added the emissions after 8 a.m.; another used a special dilution pattern.

JEFFRIES: The results you showed on the comparison, then, use a mixture of diagrams or use one diagram?

TRIJONIS: The final comparison in Houston was the standard FKMA diagram, because in Houston we found the results were insensitive to the EKMA diagram. In Los Angeles the final results were based on O_3 for radiations at fixed times, depending on the monitoring site; addition of emissions after 8 a.m.; and a special dilution pattern. Those are the three extra additions to EKMA. These were not standard; standard EKMA would not have given as good agreement as these.

JEFFRIES: So, in effect, you generated a type of city-specific diagram and then used it throughout the whole time period?

TRIJONIS: That's right, for Los Angeles.

2. EVALUATION OF THE EMPIRICAL KINETIC MODELING APPROACH AS PREDICTOR OF MAXIMUM OZONE

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ABSTRACT

The Empirical Kinetic Modeling Approach (EKMA) is a Lagrangian photochemical air quality simulation model that calculates ozone from its precursors, nonmethane organic compounds, and oxides of nitrogen. This study evaluated the performance of this approach when used to estimate the maximum ozone concentration that can occur in an urban area and its environs. The evaluation was conducted using data for St. Louis, MO, Houston, TX, Philadelphia, PA, and Los Angeles, CA.

A novel statistical evaluation procedure was developed to measure the accuracy of the EKMA ozone estimates. The accuracy parameter is defined as the ratio of observed ozone to estimated ozone. Associated with this ratio is an accuracy probability, which is defined as the probability that the ratio lies within a predefined percent (e.g., ± 20%) of unity, a unit value of the ratio denoting perfect agreement between observation and prediction. The evaluation procedure uses nonmethane organic compounds and oxides of nitrogen as inputs to calculate the accuracy probability of the EKMA ozone estimate. The full range of accuracy probabilities associated with the EKMA ozone estimates is displayed in graphical form on the nonmethane organic compound-oxides of nitrogen plane.

For St. Louis, results are presented comparing EKMA's performance for three different chemical models. A Monte Carlo method for using EKMA to predict the distribution of ozone maxima is described, and applications of the method to the design and analysis of ozone control strategies are discussed.

2. EVALUATION OF EKMA AS PREDICTOR OF MAXIMUM O_3

Martinez and Maxwell

INTRODUCTION

The Empirical Kinetic Modeling Approach (EKMA) is a Lagrangian photochemical model that calculates ozone (O_3) as a function of nonmethane organic compounds (NMOC) and oxides of nitrogen (NO_x). The EKMA approach has beem extensively documented, and we will forego discussing the technical details of the model (EPA, 1977, 1978; Dodge, 1977; Trijonis and Hunsaker, 1978; EPA, 1980; Whitten and Hogo, 1978).

This paper describes the results of a study conducted to evaluate the performance of EKMA in estimating the maximum O_3 concentration that could occur in an urban area and its environs. The study measured EKMA's ability to predict maximum O_3 and defined conditions under which O_3 estimates could achieve specific accuracy levels. The paper also summarizes the results of the evaluation for four cities: St. Louis, MO, Houston, TX, Philadelphia, PA, and Los Angeles, CA. A detailed description of the results is contained in reports by Martinez et al. (1982) and Martinez and Maxwell (1982).

METHODOLOGY

Figure 2-1 illustrates the steps of the evaluation methodology, which are described in this section.

Reference Data Set

The reference data set consisted of observed 6:00 a.m. to 9:00 a.m. local time (LT) NMOC and NO_x and the measured O_3 maximum for each day. We averaged 6:00 a.m. to 9:00 a.m. NMOC and NO_x over a group of sites located in the subregion of the urban area where their respective sources were concentrated. EKMA considers the 6:00 a.m. to 9:00 a.m. LT NMOC and NO_x to be the precursors of the maximum O_3 that occurs downwind of the emissions subregion later in the day. The observed daily O_3 maximum is defined as the highest hourly average O_3 measured from 12:00 noon to 5:00 p.m. LT at any monitoring station in the area. The timing of the O_3 maximum is dictated by EKMA's assumptions. Each reference data set contains one entry per day. The data set for St. Louis contains 100 days, for Houston, 61 days, for Philadelphia, 29 days, and for Los Angeles, 176 days. The data sets are listed in Martinez et al. (1982).

The criteria for selecting days for the reference data set consisted of: data availability, the time of occurrence of the daily O_3 maximum, and the prevalence of meteorological conditions that are necessary, but may not be sufficient, for the O_3 maximum to be at least 100 ppb. The 100-ppb cutoff ensures that all days when the O_3 national ambient air quality standard (NAAQS) of 120 ppb is exceeded are included in the evaluation data set. Such days were chosen for the evaluation for two reasons. First, EKMA is based on worst-case assumptions and therefore cannot be expected to perform well for days that do not meet these conditions. Second, because we were interested in

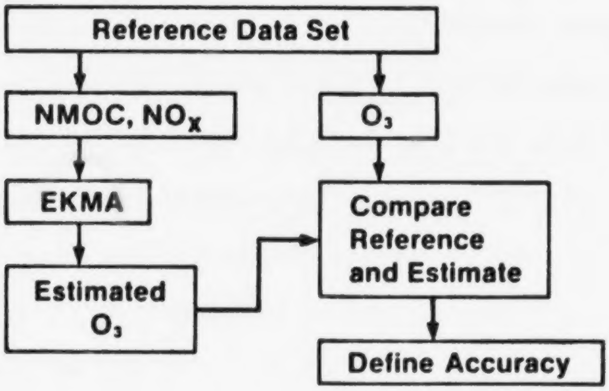

Reference Data Set
NMOC, NO_x
O_3
EKMA
Compare Reference and Estimate
Estimated O_3
Define Accuracy

Figure 2-1. Evaluation methodology used in the study.

maximum O_3 potential with respect to the NAAQS, days with conditions associated with low O_3 were not important to our evaluation.

We used the reference concentrations of 6:00 a.m. to 9:00 a.m. LT NMOC and NO_x to define an evaluation region on the NMOC-NO_x plane. (The evaluation region is defined to limit the results of the EKMA evaluation to the area of the NMOC-NO_x plane where the data are located.) Figure 2-2 shows the evaluation region for St. Louis. It was defined by regressing NO_x on NMOC and placing a band around the regression line to capture approximately 95% of the joint distribution of NMOC and NO_x. For St. Louis, the regression line is $NO_x = 0.0958\ (NMOC) + 10.4$, and the evaluation region is defined by $NO_x = 0.0958\ (NMOC) + 10.4 \pm 1.96s$, where s is the standard error of regression ($s = 16.9$ for St. Louis). For St. Louis, but not for the other three cities, we further restricted the evaluation region by omitting all points in the shaded area of Figure 2-2, in which $NMOC/NO_x < 5$. We omitted these points because in St. Louis the daily maximum O_3 is always below 100 ppb when $NMOC/NO_x < 5$. We defined evaluation regions for the remaining three cities using the same procedure.

EKMA O_3 Estimates

Basically, EKMA takes two forms -- standard EKMA and city-specific EKMA. Standard EKMA is based on conditions that prevail in the Los Angeles area, whereas the city-specific version uses model inputs for a particular city. We evaluated the performance of both forms of EKMA for each city.

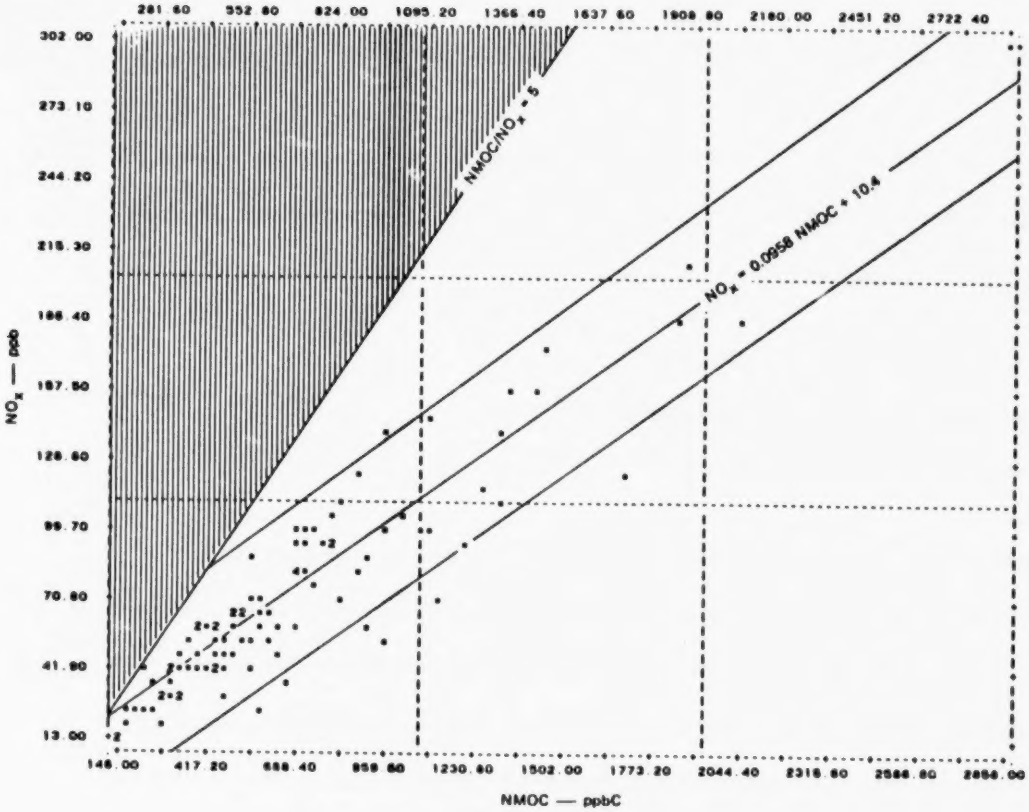


Figure 2-2. Evaluation region of the NMOC-NO_x Plane for St. Louis.

For both standard and city-specific EKMA, the inputs used to estimate O_3 were 6:00 a.m. to 9:00 a.m. LT NMOC and NO_x, spatially averaged over a specific set of monitors located in the emissions region of the city.

Statistical Evaluation of EKMA Performance

We used the ratio R = REF/EST, where REF denotes the reference daily O_3 maximum and EST the EKMA estimate, as the performance measure in evaluating EKMA. Using this ratio, we defined three accuracy regions as follows:

- Region 1: $1.2 < REF/EST$
- Region 2: $0.8 \leq REF/EST \leq 1.2$
- Region 3: $REF/EST < 0.8$

Region 1 contains ratios representing cases of substantial underprediction. We consider ratios in Region 2 to represent the most accurate predictions that can be made because the error is at most 20%, which is consistent with measurement precision. Region 3 contains ratios representing cases of substantial overprediction.

To evaluate EKMA performance, we calculated the probability that a given EKMA estimate falls in one of the three regions defined above. We made this calculation by finding a multiple linear regression equation that described the ratio R as a function of NMOC, NO_x, and other variables such as maximum daily temperature. We then used the equation for R to estimate the probabilities $P(R > 1.2)$, $P(0.8 \leq R \leq 1.2)$, and $P(R > 0.8)$, based on the assumption that the residuals of the regression fit are Gaussian. We then displayed the accuracy probabilities on graphs showing the probability as a function of NMOC and NO_x, and plotted probability isopleths on the NMOC-NO_x plane.

EKMA Evaluation

The results discussed below for St. Louis, Houston, Philadelphia, and Los Angeles pertain to EKMA with the Dodge chemical mechanism. Another section describes the EKMA evaluation for two other chemical mechanisms using St. Louis data.

Results for St. Louis

Figure 2-3 plots the standard-EKMA O_3 estimates against the reference O_3 concentrations. The figure shows the three accuracy regions. Most of the points evidently fall within Region 3. Hence, standard EKMA tends to overpredict most of the time. The figure also shows that the correlation between estimate and reference values is low, being only $r = 0.476$.

For the standard-EKMA estimates, Figure 2-4 shows the accuracy probability associated with the regression equation for R that is shown at the bottom of the figure; R is a function of $1/NMOC$, $1/NO_x$, NO_x, maximum daily temperature (denoted by T), and background O_3 (denoted by BO_3).

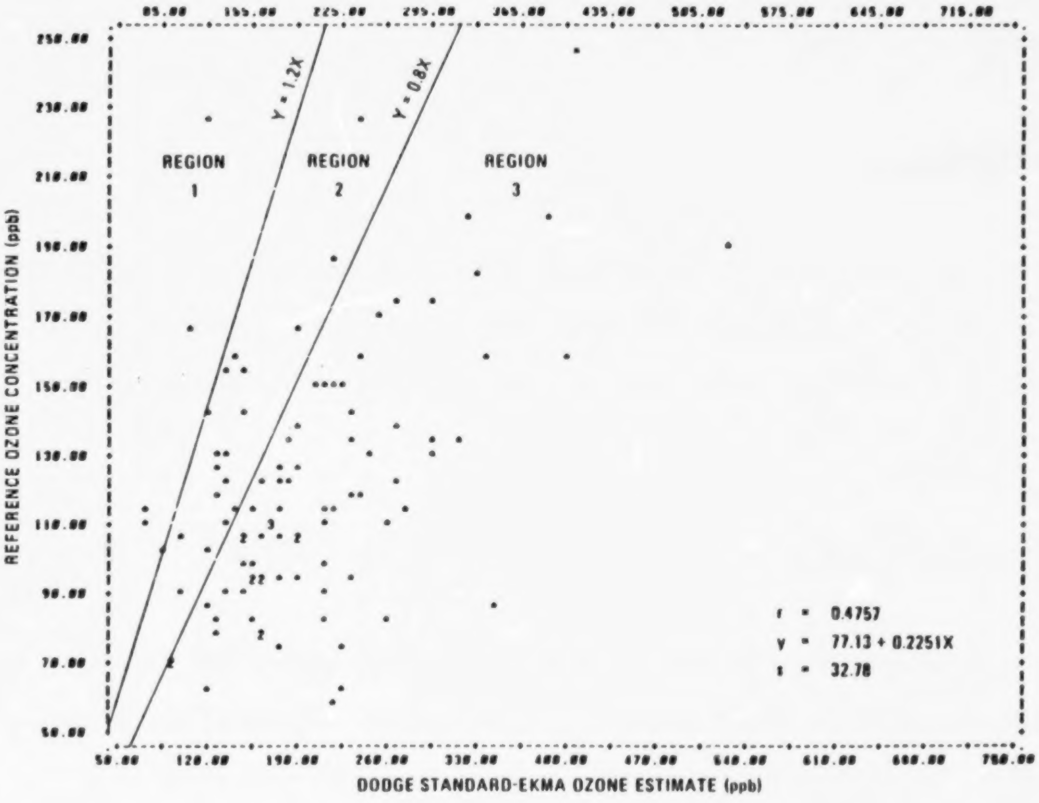
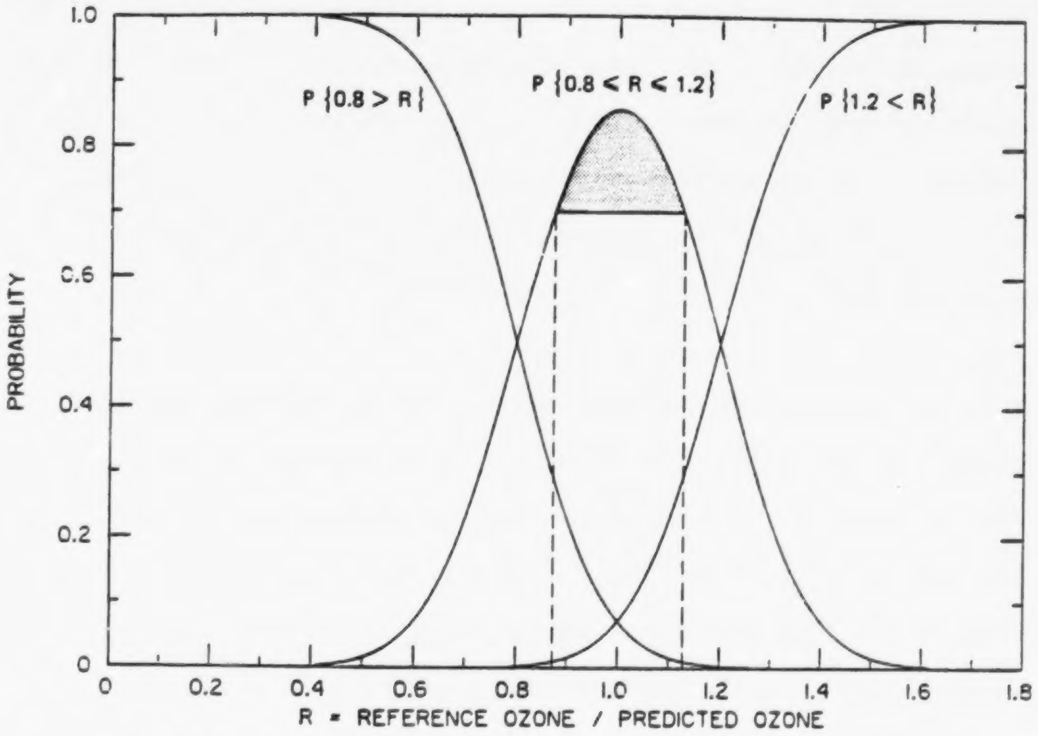


Figure 2-3. For St. Louis, standard EKMA overestimates reference O_3.



$$R = -0.6 + 88.7/NMOC + 7.6/NO_x - 0.0009\ NO_x + 0.02\ T + 0.005\ BO_3$$

Figure 2-4. Accuracy probability describes performance of standard EKMA for St. Louis.

Figure 2-4 shows that for a value of R equal to 1.0, there is about an 85% probability that the model estimate is within 20% of the reference O_3 concentration. Correspondingly, the probability that the model estimate will overpredict or underpredict the reference O_3 by at least 20% is about 8%. The two vertical dashed lines, drawn from the curve defining the probabilities for accurate predictions, define the range of R values for which there is at least a 70% probability that the EKMA estimate is within 20% of the reference O_3 concentration; these values range approximately from 0.875 to 1.12. The shaded area identifies the 70% or greater probability range for the most accurate predictions.

Figure 2-5 displays the constant-R contours on the NMOC-NO_x plane for EKMA. The evaluation region shown in the figure corresponds to that shown in Figure 2-2; it contains the range of NMOC and NO_x combinations observed in the evaluation data set. The shaded area in the figure corresponds to the shaded area in Figure 2-4. The shaded area depicts the range of NMOC, NO_x pairs for which the EKMA estimate has a 70% or greater probability of accurately predicting (within 20%) the reference O_3 concentration. Figure 2-5 shows that an accurate estimate of the reference O_3 concentration is most probable for NMOC concentrations approximately between 200 ppbC and 500 ppbC, and for NO_x concentrations approximately between 18 ppb and 50 ppb. The figure also shows that the majority of the evaluation region corresponds to R values less than 1.0 or where EKMA overpredicts the reference O_3. The region of overprediction corresponds to the large NMOC and moderate to large NO_x concentrations. The

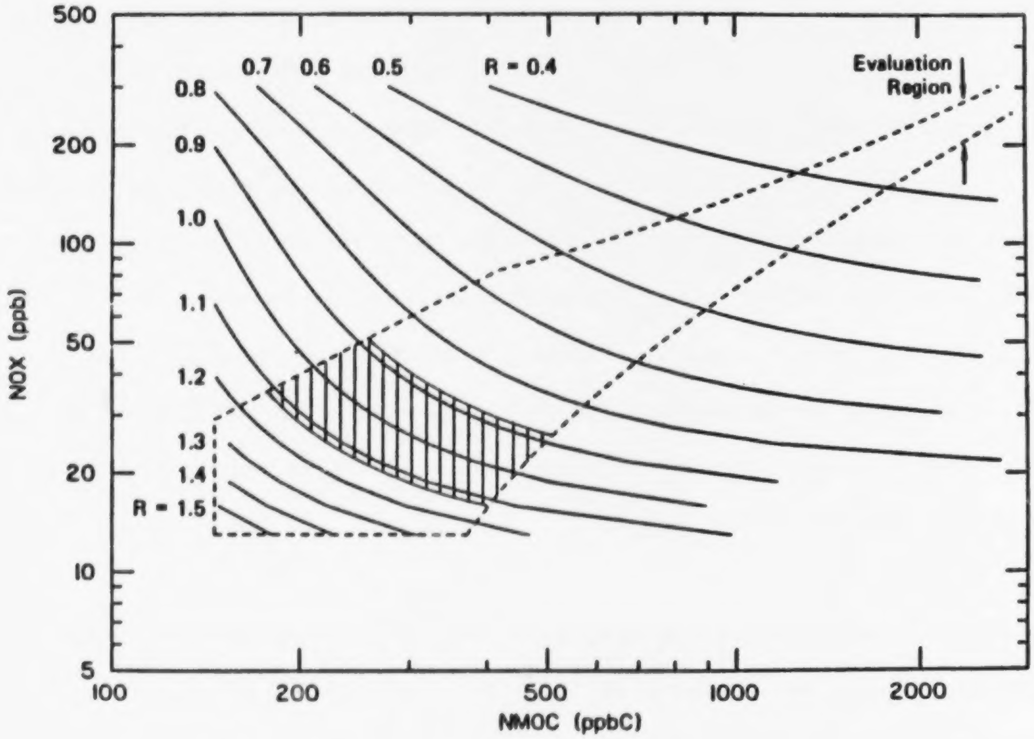


Figure 2-5. Accuracy regions define NMOC and NO_x values associated with standard-EKMA predictions for St. Louis.

region where the model underpredicts, $R > 1.2$, is relatively small, and the range of NMOC and NO_x concentrations that will result in underpredictions is small.

Figure 2-6 depicts the reference O_3 plotted against the city-specific EKMA estimates. Compared with Figure 2-3 for standard EKMA, Figure 2-6 shows a much larger percentage of points in Region 2 ($0.8 \leq R \leq 1.2$), which is the region of accurate predictions. There are also more points in Region 1, where the model estimates underpredict the reference O_3, and, consequently, there are fewer points in Region 3, the overprediction region. However, the majority of the points are still in Region 3, which indicates that city-specific EKMA tends to overpredict the reference O_3, though not as much as standard EKMA. The correlation coefficient ($r = 0.470$) is very close to that for standard EKMA ($r = 0.476$).

Figure 2-7 is a plot of the constant-R contours on the NMOC-NO_x plane for city-specific EKMA. The equation for R is shown at the bottom of Figure 2-7. In contrast to the R-equation for standard EKMA (see Figure 2-4), R for city-specific EKMA does not include $1/NO_x$ as one of the independent variables.

The shaded region of Figure 2-7 corresponds to the area for which the probability $P(0.8 \leq R \leq 1.2)$ is at least 70%. The shaded region contains NMOC concentrations ranging approximately between 240 ppbC and 500 ppbC along with NO_x concentrations in the range of 14 ppb to 70 ppb. Compared with Figure 2-5 for standard EKMA, the size of the shaded area has increased. The

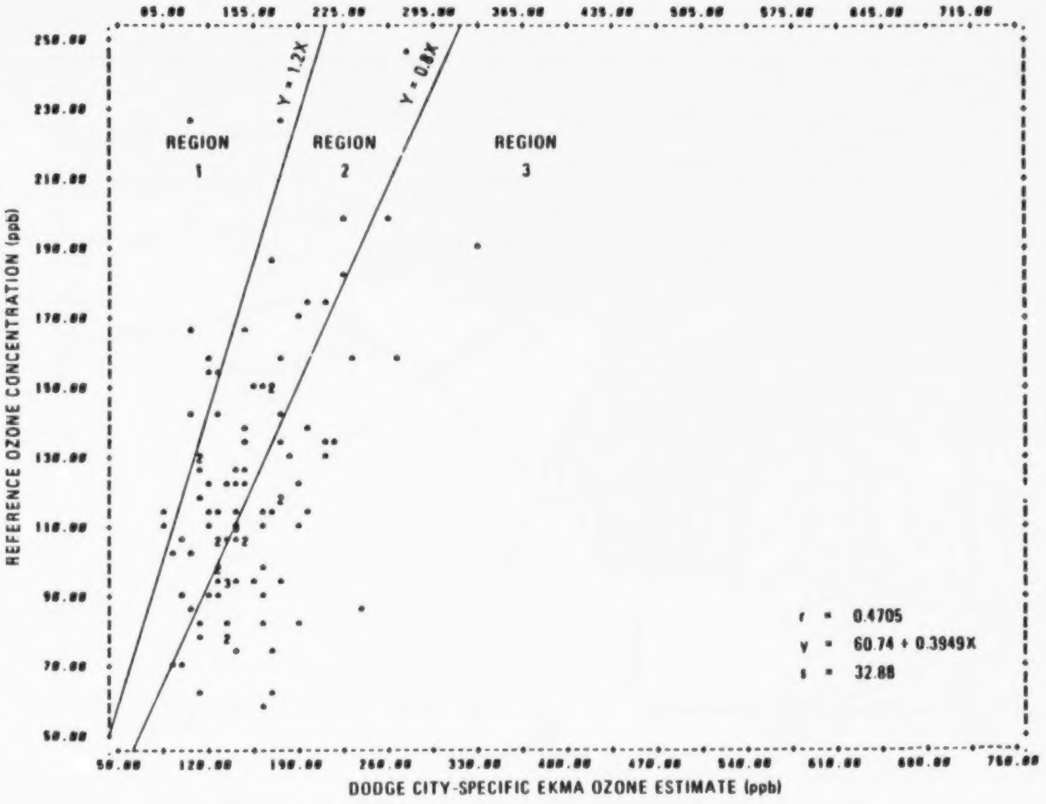
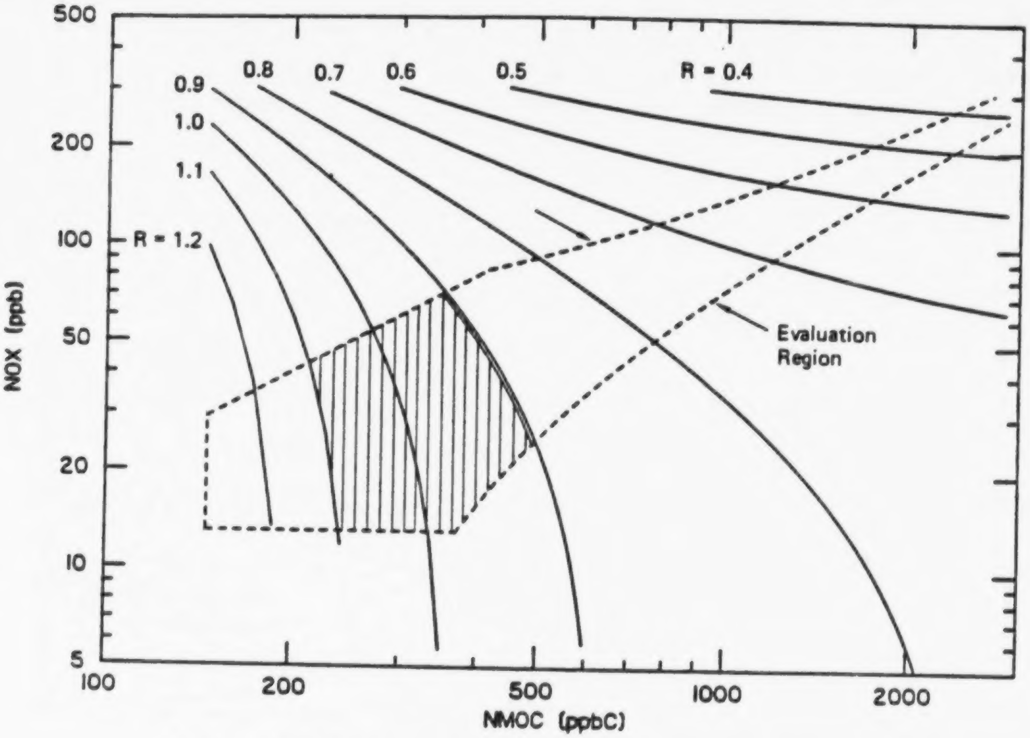


Figure 2-6. City-specific EKMA estimates for St. Louis tend to be more accurate.



$$R = -0.5 + 84.8/NMOC - 0.002\ NO_x + 0.03\ T + 0.006\ BO_3$$

Figure 2-7. Region of high accuracy probability is larger for city-specific than for standard EKMA for St. Louis.

range of NMOC concentrations, which for standard EKMA was from 200 ppbC to 500 ppbC, has decreased, but the range of NO_x concentrations (previously between 18 ppb and 50 ppb) increased. As was found for standard EKMA, the majority of the evaluation region results in overpredictions ($R < 1.0$) of reference O_3. Conversely, there is a small range of NMOC and NO_x concentrations that will result in underpredictions ($R > 1.2$).

Results for Houston

Figure 2-8 shows a scatterplot of observed (OBS) and estimated (EST) O_3 for the Houston Area Oxidant Study (HAOS) data set. Region 1 contains two points, Region 2 has 11, and Region 3 has 48. (One of the points in Region 2 is plotted just below the line OBS = 0.8 EST.) Thus, about 3% of the cases are underpredicted, and the remainder satisfy the inequality $OBS \leq 1.2\ EST$. These percentages are similar to those previously obtained for St. Louis (see Figure 2-3).

A multiple regression equation was derived for R = OBS/EST as a function of NMOC and temperature difference (denoted by DT) for the HAOS data set; the equation for R is shown at the bottom of Figure 2-9. The multiple correlation coefficient is $r = 0.63$ and the standard error of the regression is $s = 0.25$. The significance level of the regression and of the coefficients of NMOC and DT is $p < 0.0001$, but the constant term is not statistically significant at the 0.05 level.

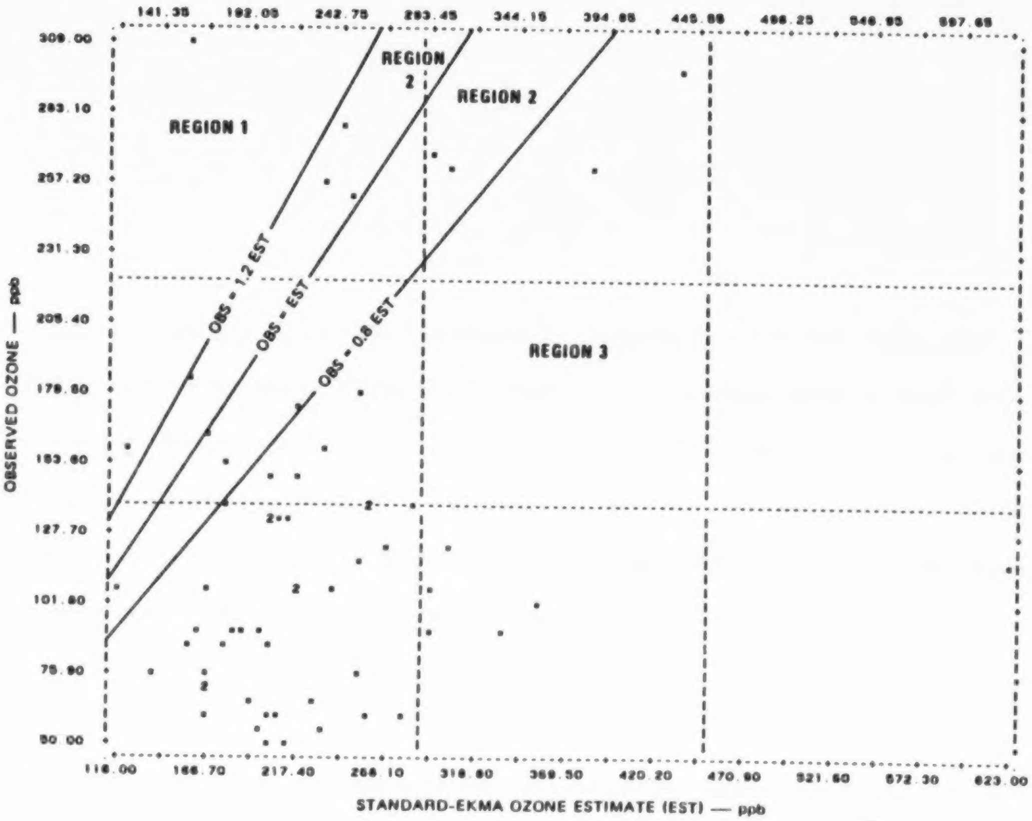
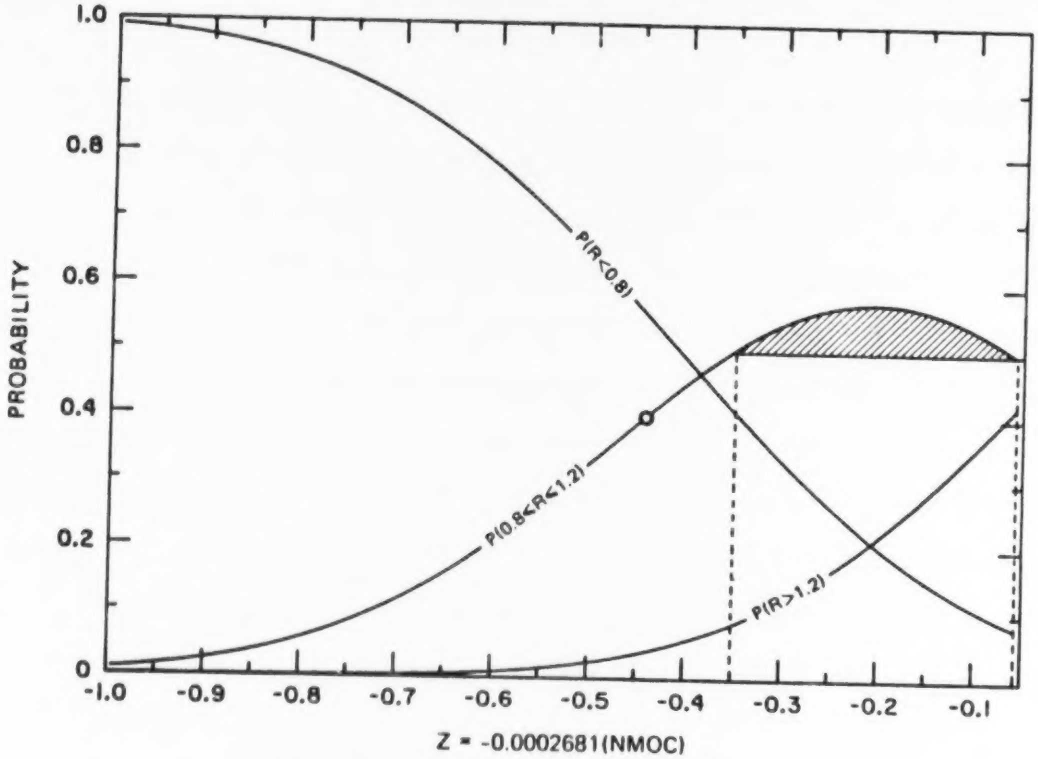


Figure 2-8. Standard EKMA produced substantial overprediction for Houston (HAOS).

Figure 2-9 displays the probability curves for the three accuracy regions as a function of the variable $Z = -0.0002681$ (NMOC). The figure shows that $P(R \leq 1.2) > 0.5$ for $Z < -0.175$, which corresponds to NMOC > 654 ppbC. This reflects standard EKMA's tendency to overpredict.

Figure 2-9 shows that the curve for $P(0.8 \leq R \leq 1.2)$ is flattened and spread out, in sharp contrast to the relatively narrow curve shown for St. Louis in Figure 2-4. (Note, however, that the horizontal axes are not scaled equally in Figures 2-4 and 2-9.) The maximum value of $P(0.8 \leq R \leq 1.2)$ is 0.58 in Figure 2-9, compared to the maximum of 0.83 in Figure 2-4. The curves in Figures 2-4 and 2-9 differ in shape because the standard error of the regression is smaller for the St. Louis data ($s = 0.15$) than for the Houston data ($s = 0.25$). The maximum probability of 0.58 in Figure 2-9 occurs in the neighborhood of $Z = -0.21$, which corresponds to NMOC = 723 ppbC. The shaded region in Figure 2-9 is where $P(0.8 \leq R \leq 1.2) \geq 0.50$ and is defined by $-0.35 < Z < -0.060$, which corresponds to 224 ppbC < NMOC < 1305 ppbC.

Figure 2-10 displays constant-Z lines on the NMOC-NO_x plane, along with the evaluation region for the Houston data. The shaded area corresponds to the region where $P(0.8 \leq R \leq 1.2) \geq 0.50$. Inside the evaluation region, NMOC, NO_x combinations that fall within and to the right of the shaded area satisfy the inequality $P(R \leq 1.2) > 0.60$. Points to the left of the shaded area satisfy the relation $P(R > 1.2) > 0.42$, and thus are more likely to yield underestimates of observed O_3. The tendency of standard EKMA to overpredict



$$R = 0.1 \underbrace{- 0.0002681\ NMOC}_{Z} + 0.06\ DT$$

Figure 2-9. Probability of an accurate prediction is less than 0.6 for standard EKMA for HAOS.

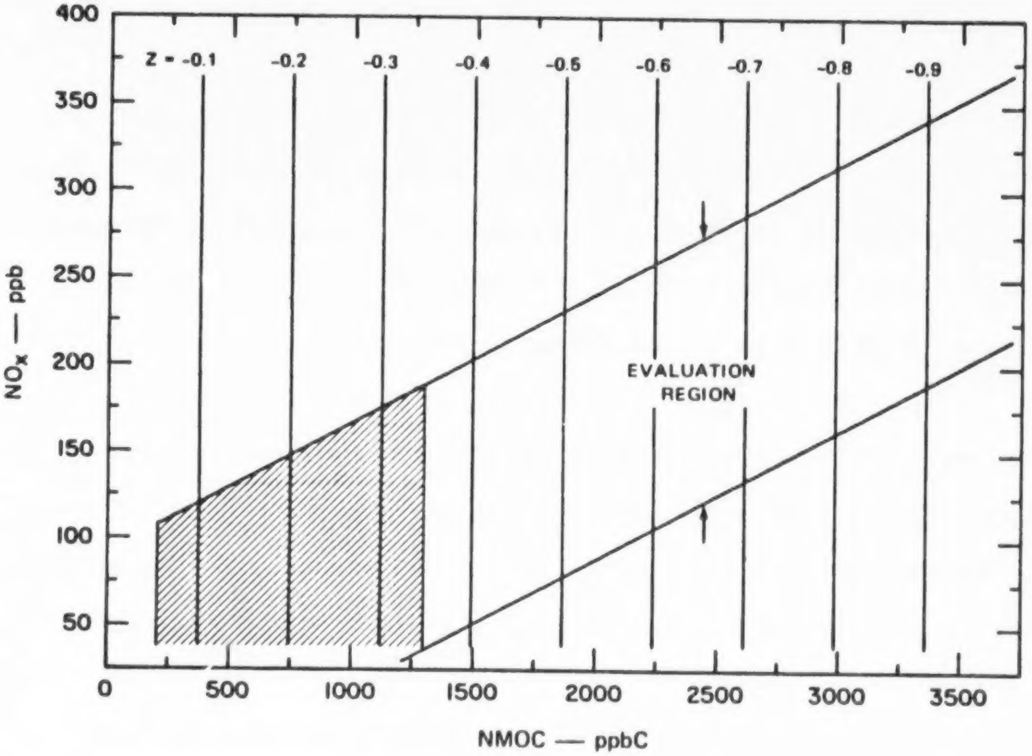


Figure 2-10. Region of overprediction includes most of the evaluation region for standard EKMA for HAOS.

O_3 is reflected in the large difference in the respective sizes of the regions that flank the shaded area in Figure 2-10.

Figure 2-11 shows a scatterplot of observed and estimated O_3 for the HAOS data. Whereas the standard-EKMA estimates demonstrate a marked tendency to overpredict, the city-specific estimates demonstrate the opposite. The majority of the points in the figure are in Region 1, the region of underprediction. For the HAOS data, Figure 2-11 has 33 points (54%) in Region 1, 16 points (26%) in Region 2, and 12 points (20%) in Region 3. Observed and estimated O_3 are correlated for the HAOS data; the correlation is low ($r = 0.24$) but statistically significant ($p < 0.04$).

We derived a multiple regression equation for the ratio $R = OBS/EST$ for the HAOS data set. The equation is shown at the bottom of Figure 2-12, and, as for standard EKMA, it shows R as a function of NMOC and DT. The multiple correlation coefficient is $r = 0.65$, and the standard error is $s = 0.60$.

Figure 2-12 displays the probability curves for the three accuracy regions as a function of the variable $Z = -0.0006191$ (NMOC). The curves are computed for DT = 11.6°C, which is its mean value. The probability $P(R \leqslant 1.2)$ exceeds 0.5 for $Z < -0.90$, which corresponds to NMOC > 1454 ppbC. Thus, the city-specific O_3 estimates can be considered to be upper bounds generally for high values of NMOC. The curve for $P(0.8 \leqslant R \leqslant 1.2)$ covers the entire range of NMOC concentrations, but the probability is low that a given NMOC value will fall in Region 2. The highest probability of an accurate prediction is

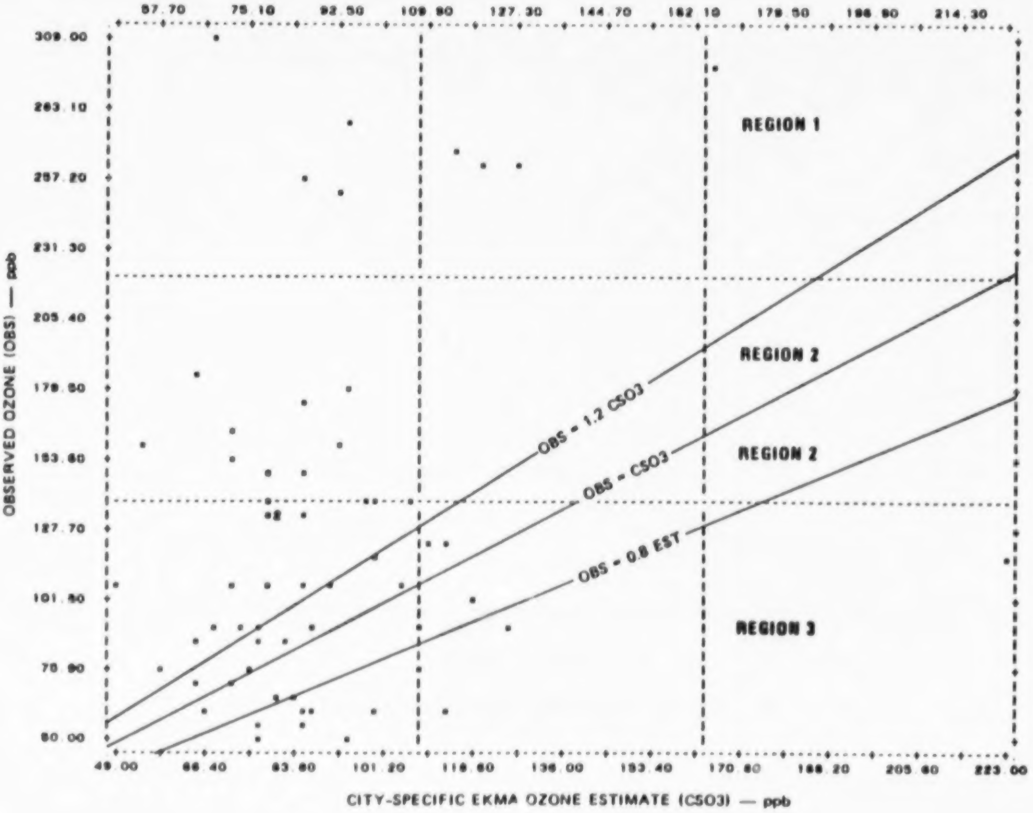
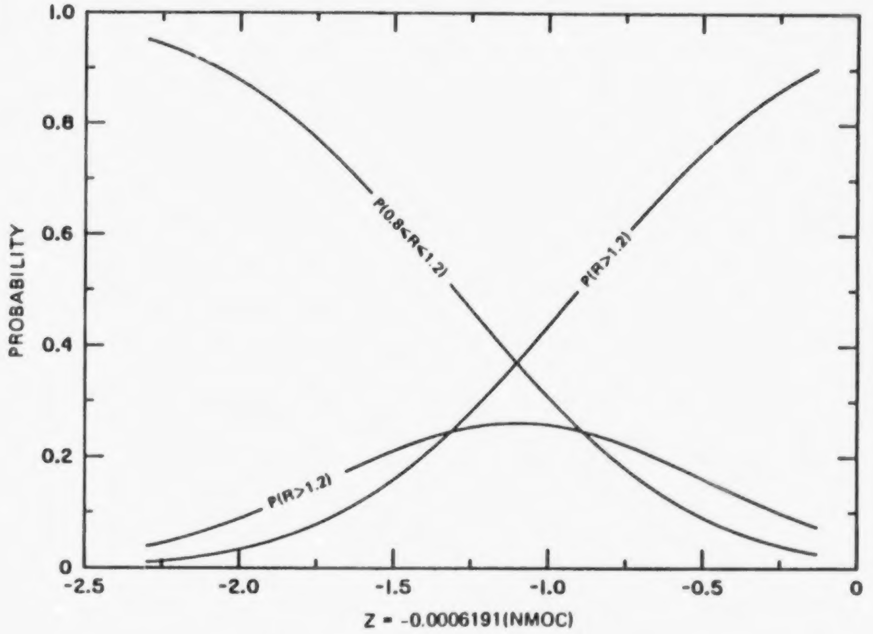


Figure 2-11. City-specific EKMA underpredicted substantially for HAOS.



$$\mathbf{R = 0.2 \underbrace{- 0.0006191\ NMOC}_{Z} + 0.2\ DT}$$

Figure 2-12. Accurate estimates have a low probability for city-specific FKMA for HAOS.

about 0.26, and occurs for $Z = -1.11$, which corresponds approximately to NMOC = 1793 ppbC.

For the HAOS data, EKMA substantially overpredicted in the standard mode, and underpredicted in the city-specific mode. As a result, the probability of an accurate prediction for the HAOS data was generally low. In general, it appears that in either mode EKMA tends to be a low-accuracy predictor of O_3 for the Houston area.

Results for Philadelphia

Figure 2-13 shows a scatterplot of observed O_3 and standard-EKMA O_3 estimates. Of the 29 points plotted, 4 (14%) are in Region 1, 5 (17%) are in Region 2, and the remainder are in Region 3. Note, however, that the four points in Region 1 are not grossly underpredicted.

Thus, as in St. Louis and Houston, standard EKMA shows a marked tendency to overpredict. Unlike the St. Louis case, there is no statistically significant correlation between observed and estimated O_3.

The multiple regression equation derived for the ratio $R = OBS/EST$ is shown at the bottom of Figure 2-14; R is a function of 1/NMOC and daily maximum temperature (T).

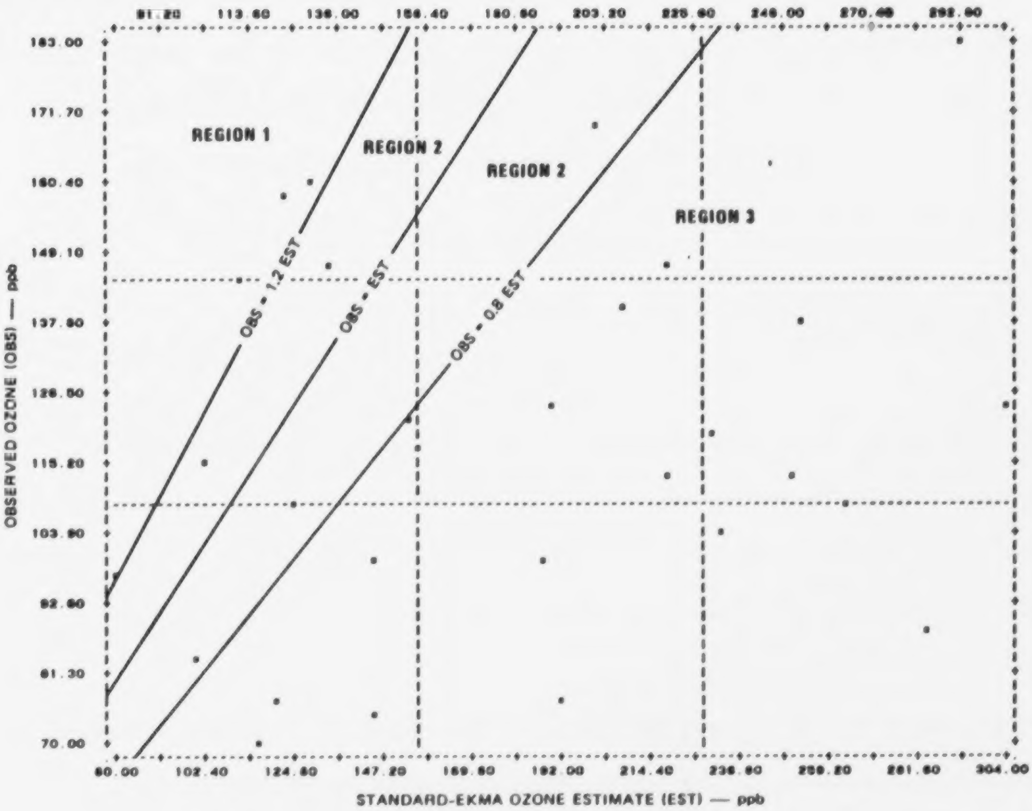
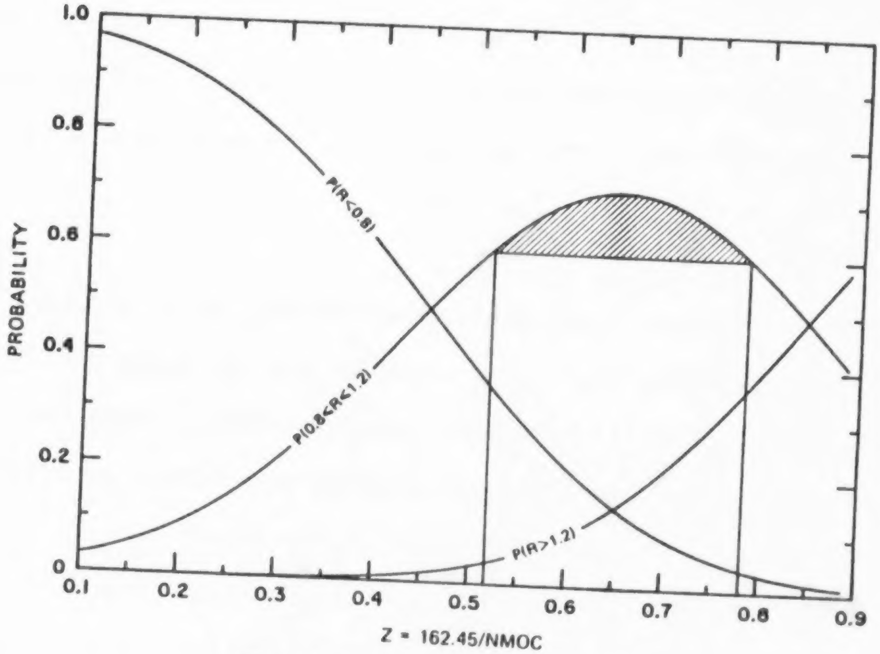


Figure 2-13. Standard EKMA for Philadelphia tends to overpredict.

Figure 2-14 displays the accuracy probability plot for R as a function of Z = 162.45/NMOC for the mean value of T, which is 27.5°C. The probability $P(R \leq 1.2)$ exceeds 0.5 for $Z < 0.85$, which corresponds to NMOC > 191 ppbC. The shaded area in Figure 2-14 defines the region with the highest probability of an accurate prediction, i.e., where $0.8 \leq OBS/EST \leq 1.2$. In the shaded area, the maximum probability is approximately 0.71, and occurs for Z = 0.65, which corresponds to NMOC = 250 ppbC. For the shaded area the variable Z is bounded by $0.51 < Z < 0.79$, for $P(0.8 \leq R < 1.2) > 0.6$.

The accuracy regions are illustrated in the NMOC-NO_x plane in Figure 2-15. The shaded area of the figure corresponds to that in Figure 2-14 and is defined by 206 ppbC < NMOC < 319 ppbC; NMOC, NO_x combinations within the shaded area have the highest probability of yielding an accurate O_3 estimate. Values of NMOC and NO_x to the right of the shaded area have a high probability that the ratio OBS/EST < 0.8; hence, this is the region of overprediction. Underprediction is most probable in the thin slice to the left of the shaded area. Thus, the vast majority of the evaluation region is associated with OBS/EST ratios smaller than 1.2.

The accuracy regions for city-specific-EKMA estimates are displayed on the NMOC-NO_x plane in Figure 2-16. The shaded area of this figure corresponds to the O_3 estimates that have the highest probability of being most accurate. The region where $R \leq 1.2$ includes the shaded area and all of the evaluation region to the right of the shaded area. Only a very narrow slice of the NMOC-NO_x plane to the left of the shaded area corresponds to the region of



$$R = -0.7 + \underbrace{162.45/NMOC}_{Z} + 0.04\ T$$

Figure 2-14. Probability of accurate predictions is moderately high for standard EKMA for Philadelphia.

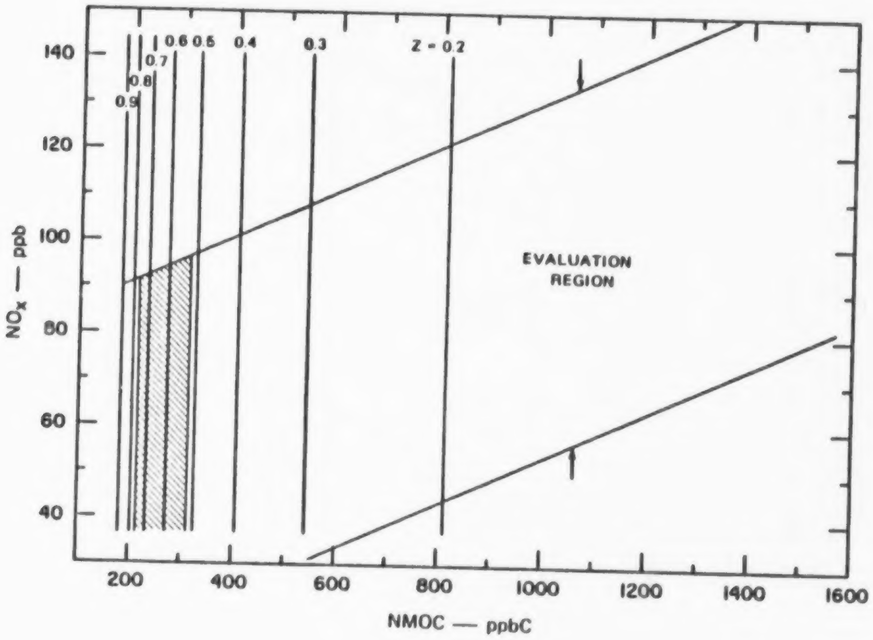
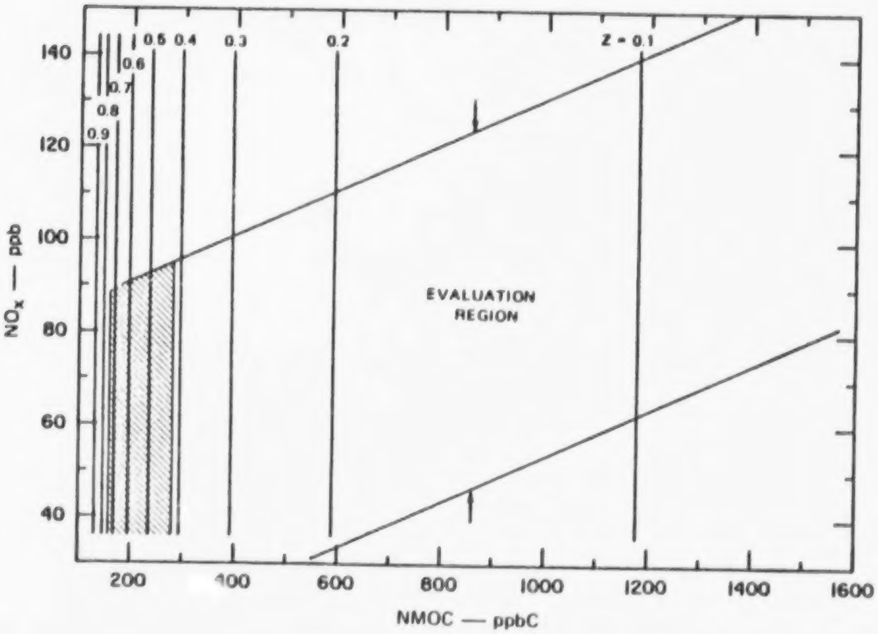


Figure 2-15. High NMOC concentrations yield overpredictions for standard EKMA for Philadelphia.



$$R = -0.6 + \underbrace{117.7/\text{NMOC}}_{Z} + 0.04\,T$$

Figure 2-16. City-specific and standard-EKMA estimates for Philadelphia were very similar.

of underprediction, and that slice is actually outside the bounds of the evaluation region.

For Philadelphia, the standard- and city-specific-EKMA O_3 estimates were very similar. However, in a reversal of roles from the St. Louis and Houston cases, the Philadelphia city-specific estimates were more accurate and also displayed a lower tendency toward underprediction than did the standard-EKMA estimates. However, in keeping with previous results, the standard-EKMA O_3 estimates showed a pronounced tendency toward overprediction.

Results for Los Angeles

Figure 2-17 is a scatterplot of OBS and EST for Los Angeles. As the scatter suggests, no statistically significant correlation exists between observation and prediction. Nevertheless, the distribution of the points among the three accuracy regions is of interest. Region 1 contains 62 points (35%), Region 2 has 51 (29%), and Region 3 has 63 (36%). Thus, overpredictions, underpredictions, and accurate predictions are about equally probable. This is surprising because standard EKMA is supposed to simulate worst-case O_3 conditions in the Los Angeles area.

A multiple regression equation was derived for the ratio R = OBS/EST as a function of several variables: the equation is shown at the bottom of Figure 2-18. R is a function of $1/NO_x$, NMOC, and 1/NMOC, and maximum daily

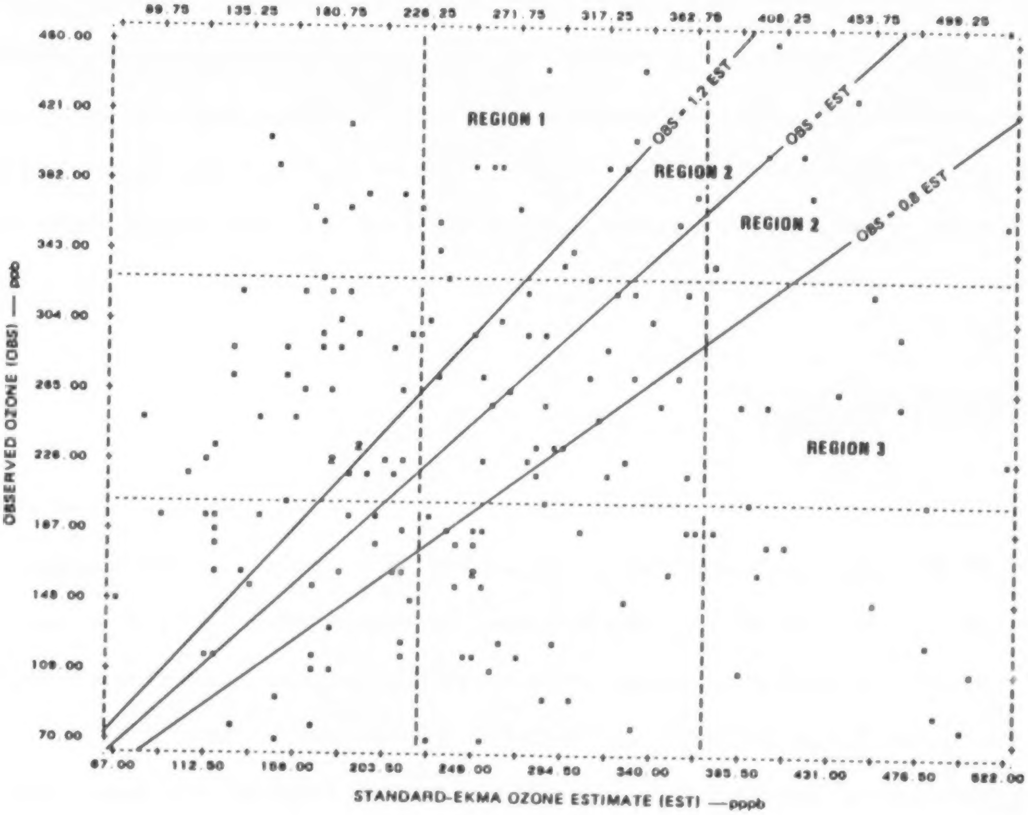
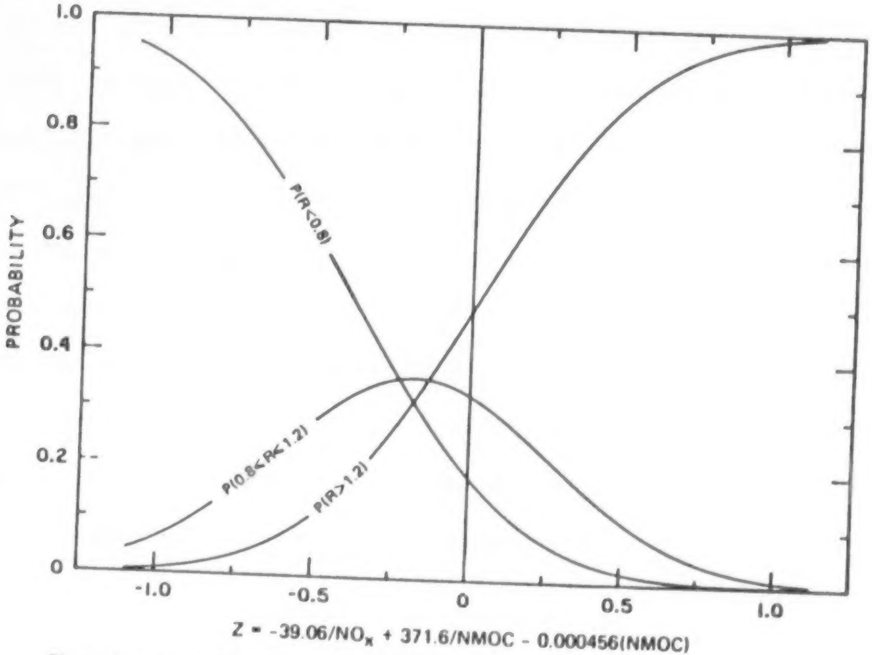


Figure 2-17. Standard-EKMA estimates for Los Angeles fell in each region in equal proportions.



$$R = -0.2 - \underbrace{39.06/NO_x + 371.6/NMOC - 0.000456\ NMOC}_{Z} + 0.02\ T$$

Figure 2-18. Under, over, and accurate predictions have similar probabilities for standard EKMA for Los Angeles.

temperature (T). The multiple regression coefficient is $r = 0.68$, and the standard error of the regression is $s = 0.43$.

The equation for R in Figure 2-18 resembles that for St. Louis in Figure 2-4 because it includes both 1/NMOC and $1/NO_x$. However, for St. Louis, these two variables had positive coefficients, which is not the case for Los Angeles. Another difference between the equation for St. Louis and that for Los Angeles is that the latter includes NMOC; despite the fact that 1/NMOC, $1/NO_x$, and NMOC are correlated, the latter two variables increase the amount of variance explained. By far the most important variable in terms of amount of variances explained is 1/NMOC, which by itself explains about 40% of the variance. The remaining three variables -- T, NMOC, and $1/NO_x$ together add another 6% to the total explained variance. Thus, NMOC or its reciprocal continues to play a large role in explaining the predictive performance of EKMA.

Figure 2-18 displays a plot of the accuracy probability derived from the expression for R as a function of the variable Z, which is defined in the figure. Reflecting the indications of Figure 2-17, Figure 2-18 shows that the probability of an accurate prediction is relatively low, with $P(0.8 \leq R \leq 1.2) < 0.37$. Moreover, the magnitude of the three probabilities is about the same in the neighborhood where $P(0.8 \leq R \leq 1.2)$ has its maximum. Thus, relatively small changes in the value of Z in this neighborhood can radically shift the probability of overprediction or underprediction. The steepness of the curves for $P(R < 0.8)$ and for $P(R > 1.2)$ suggests a similarly sensitive behavior in the overprediction and underprediction regimes, respectively. The sensitivity of the probabilities causes the standard-EKMA O_3 estimates to be of limited usefulness for obtaining upper bounds for O_3 in Los Angeles.

Figure 2-19 shows a scatterplot of observed O_3 and the city-specific EKMA estimate. In contrast to Figure 2-17, Figure 2-19 has a preponderance of overpredictions and few underpredictions. Region 1 contains six points (3% of the total), Region 2 has 25 (14%), and Region 3 has 145 (83%). Thus, the number of underpredictions has been reduced by more than a factor of 10, but the number of accurate predictions has decreased by a factor of 2.

Figure 2-20 shows the multiple regression equation derived for the ratio R = OBS/EST for the city-specific case. The equation for R in Figure 2-20 differs from that in Figure 2-17 in the presence of the variable NO_x in the former instead of the NMOC that appeared in the latter. Nevertheless, in both equations, 1/NMOC explained approximately the same amount of variance, 37% in Figure 2-20 and 40% in Figure 2-17.

Constant-Z contours are displayed on the NMOC-NO_x plane in Figure 2-21. The shaded area of Figure 2-21 corresponds to the interval $0.1 < Z < 0.3$, in which $P(0.8 \leq R \leq 1.2) > 0.60$. Thus, NMOC, NO_x combinations in the shaded area have the highest probability of yielding accurate estimates. The small area to the left of the shaded slice is the region where underprediction becomes more probable. The part of the evaluation region to the right of the shaded area is associated with an increasing probability of overprediction.

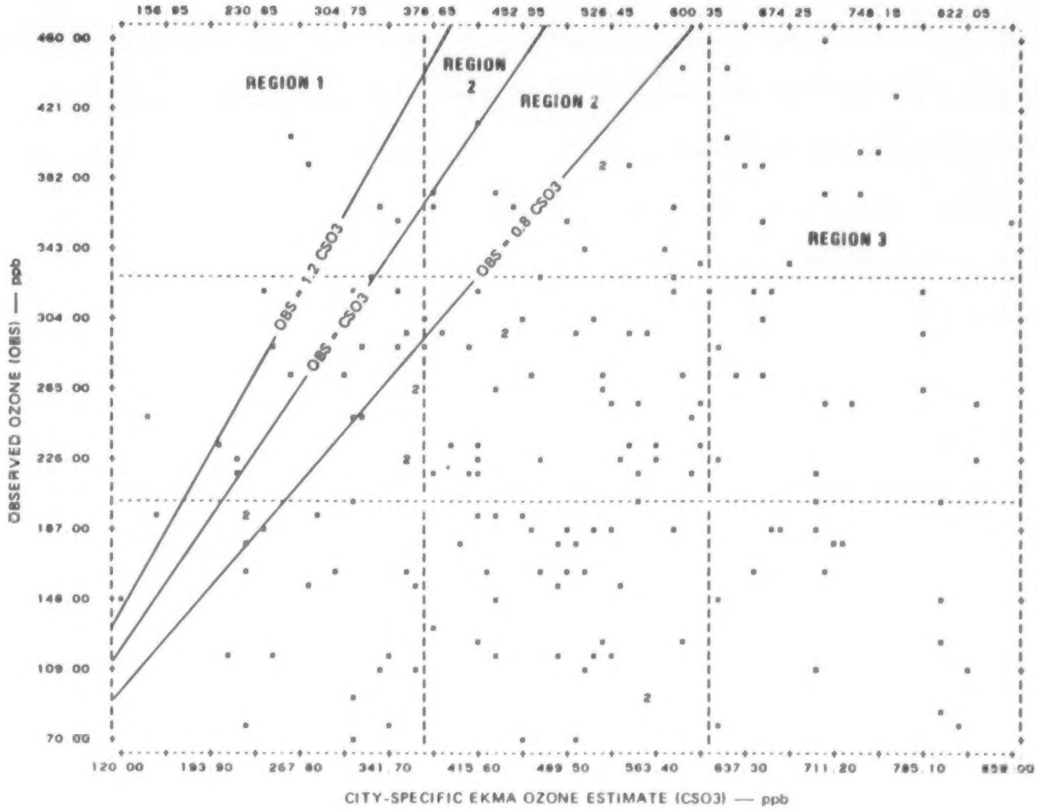
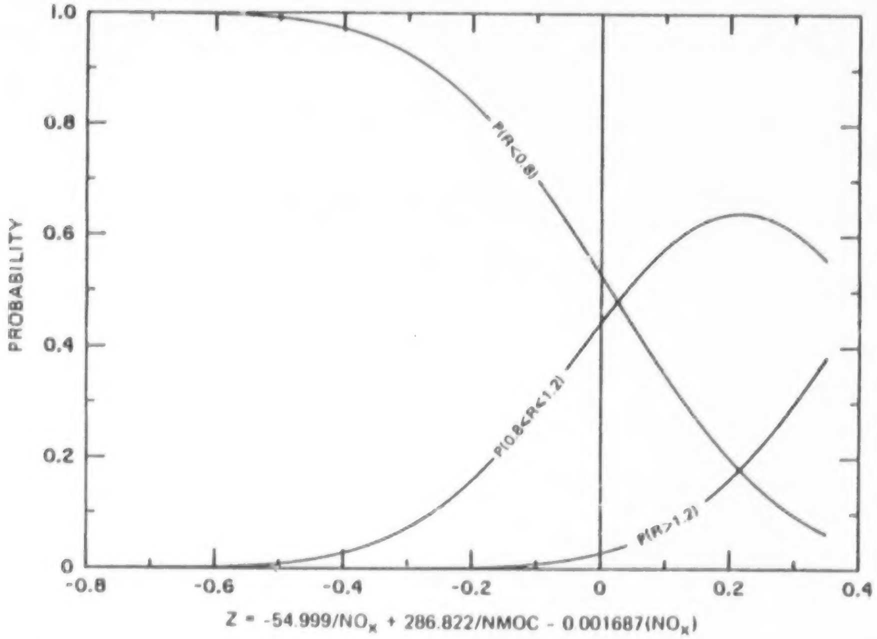


Figure 2-19. City-specific EKMA for Los Angeles overpredicts substantially.



$$R = 0.08 - \underbrace{54.999/NO_x + 286.322/NMOC - 0.001687\ NO_x}_{Z} + 0.009\ T$$

Figure 2-20. Accurate predictions are most probable for $0.1 < Z < 0.3$ for city-specific EKMA for Los Angeles.

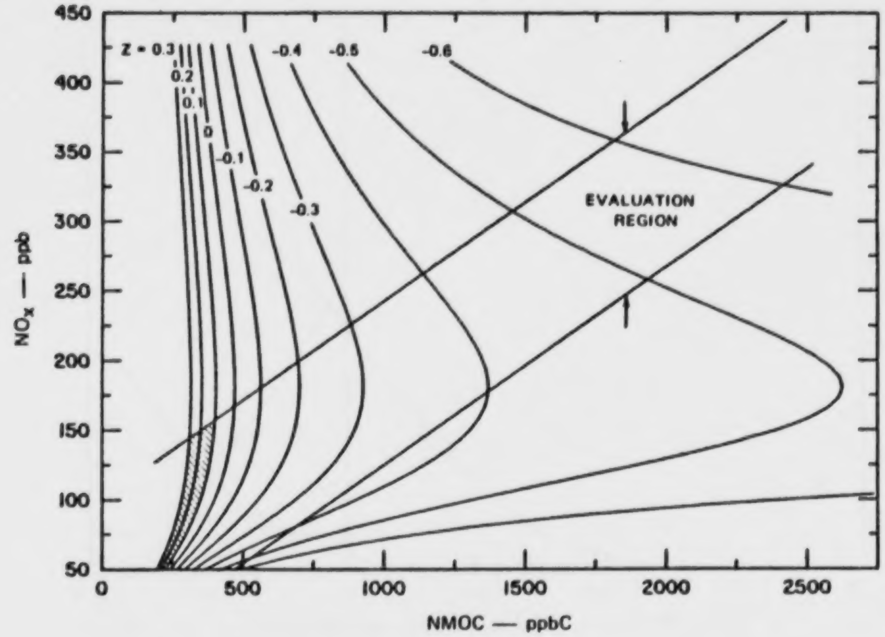


Figure 2-21. Most NMOC and NO_x lead to overprediction for city-specific EKMA for Los Angeles.

The tendency toward overprediction is thus made apparent, because most of the evaluation region is to the right of the shaded area.

That the standard EKMA yielded so many underestimates was surprising, indicating that the worst-case conditions supposedly embodied in standard EKMA do not in fact define a worst case. The city-specific EKMA, by contrast, yielded a large majority of overestimates. This suggests that the city-specific EKMA is the operational mode of choice for the purpose of obtaining an upper bound for O_3, although the magnitude of the overprediction can be very large.

DISCUSSION

The results of the EKMA evaluation for the four test cities indicate that it is feasible to use EKMA to estimate maximum O_3 because:

- Predictive accuracy is a function of NMOC and NO_x, hence, can be estimated in advance.
- Different data bases produce similar patterns of predictive accuracy, with NMOC being the most important explanatory variable.
- Evaluation methodology can be extended to other urban areas.

Three levels of accuracy were defined based on the ratio R = reference/estimated -- $R > 1.2$, $0.8 \leq R \leq 1.2$, and $R < 0.8$. The interval $R > 1.2$ defines cases of underestimation; $R < 0.8$ defines cases of overprediction. The closed interval $0.8 \leq R \leq 1.2$ defines the most accurate estimates. The accuracy of the O_3 estimates depended not only on the level of pollutant and meteorological variables, but also on whether standard or city-specific EKMA was used. Moreover, the frequency of occurrence of O_3 estimates that fell in each of the three accuracy intervals was different for all the data sets studied. Nevertheless, a general pattern emerged that relates low, medium, and high values of NMOC and NO_x to the three accuracy intervals. Low values tended to yield $R > 1.2$, medium values, $0.8 \leq R \leq 1.2$, and high values, $R < 0.8$. The precise values of NMOC and NO_x that mark the boundaries of the three accuracy intervals differed among the individual data sets. St. Louis and Houston exhibited a general trend toward a high frequency of overestimation, and a low frequency of underprediction, for the standard EKMA. Although for St. Louis and Houston standard EKMA yielded estimates in the interval $0.8 \leq R \leq 1.2$, the frequency was low, and the range of NMOC and NO_x values that produced such estimates with high probability was narrow.

The situation was different for city-specific EKMA, which tended to have a higher frequency of estimates in the interval $0.8 \leq R \leq 1.2$. City-specific EKMA also tended to underpredict more frequently, and to overpredict less frequently, than standard EKMA. Thus, although city-specific EKMA offers a higher probability of producing an accurate estimate (for which $0.8 \leq R \leq 1.2$) standard EKMA has a higher probability of yielding an upper-bound estimate (for which $R \leq 1.2$).

We regard the evaluation methodology developed in the study as an important contribution. The methods are general, and the numerical results reported are real-life examples of what can be accomplished with these techniques. In the future, this methodology can be applied to other data bases to extend and generalize the results reported here.

COMPARISON OF CHEMICAL MECHANISMS

Three different chemical mechanisms were used with EKMA, and the model's response was evaluated using St. Louis data. The three mechanisms are:

- Dodge
- Carbon Bond II (CBII)
- Demerjian (DM)

These mechanisms have been described by Jeffries et al. (1981).

Figures 2-22 and 2-23 plot the CBII and DM standard-EKMA estimates against the reference O_3. It is apparent that the CBII and DM mechanisms yield similar estimates that exhibit a stronger tendency to overpredict than the Dodge estimates (Figure 2-3).

Table 2-1 compares the number of points in the accuracy regions for the three models. The table shows that most of the data points are in Region 3, which indicates that the models strongly tend to overpredict the reference O_3 concentration. The CBII and DM models overpredicted with greater frequencies than did the Dodge model. The Dodge model had more than twice as many predictions in the accurate region (Region 2) than did the CBII model, and nearly six times as many as the DM model. The CBII and DM models each had

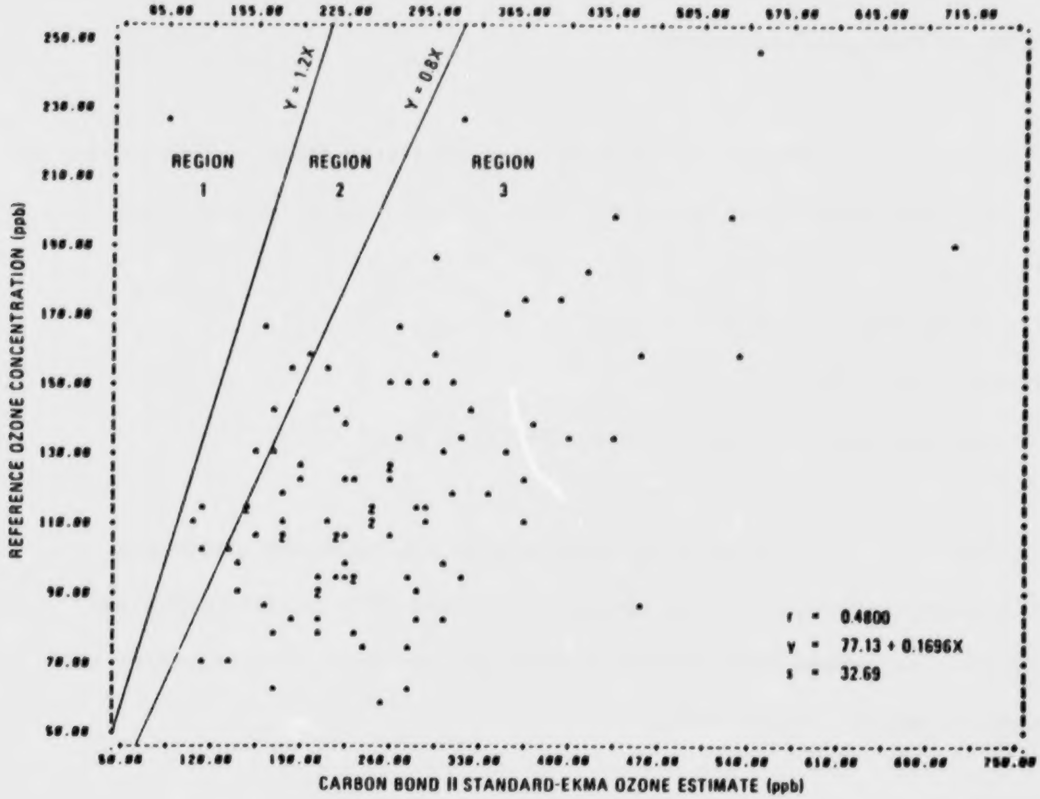


Figure 2-22. Standard EKMA with CBII overpredicts more than Dodge.

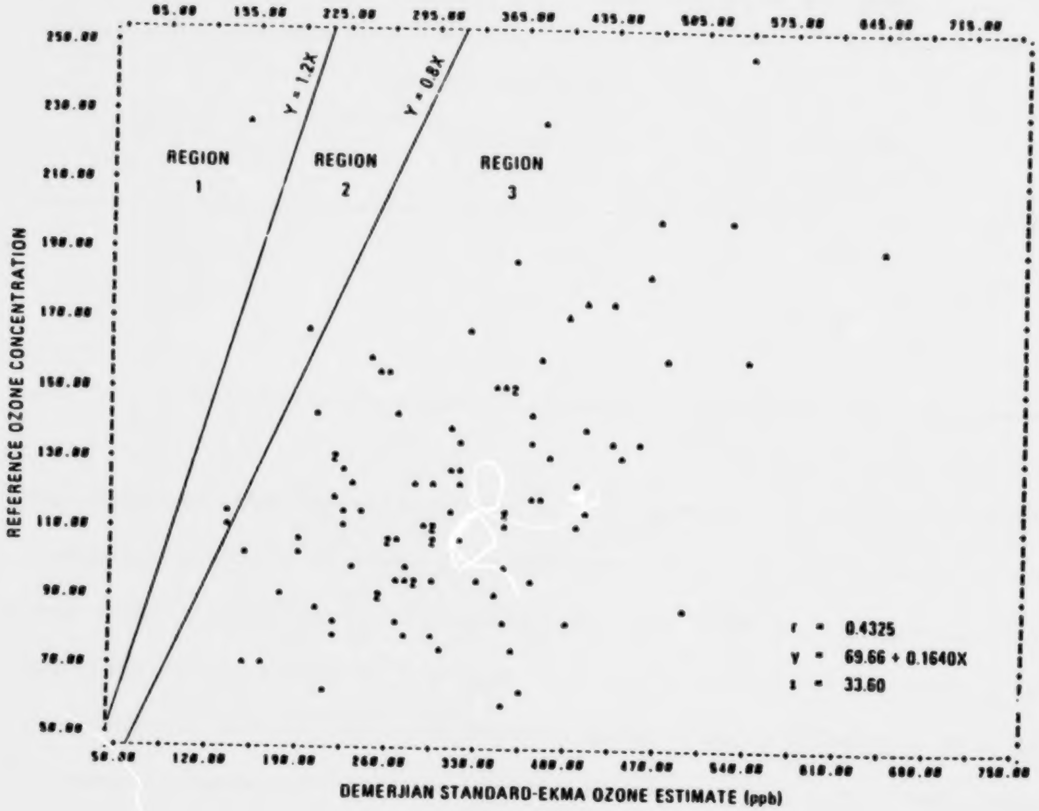


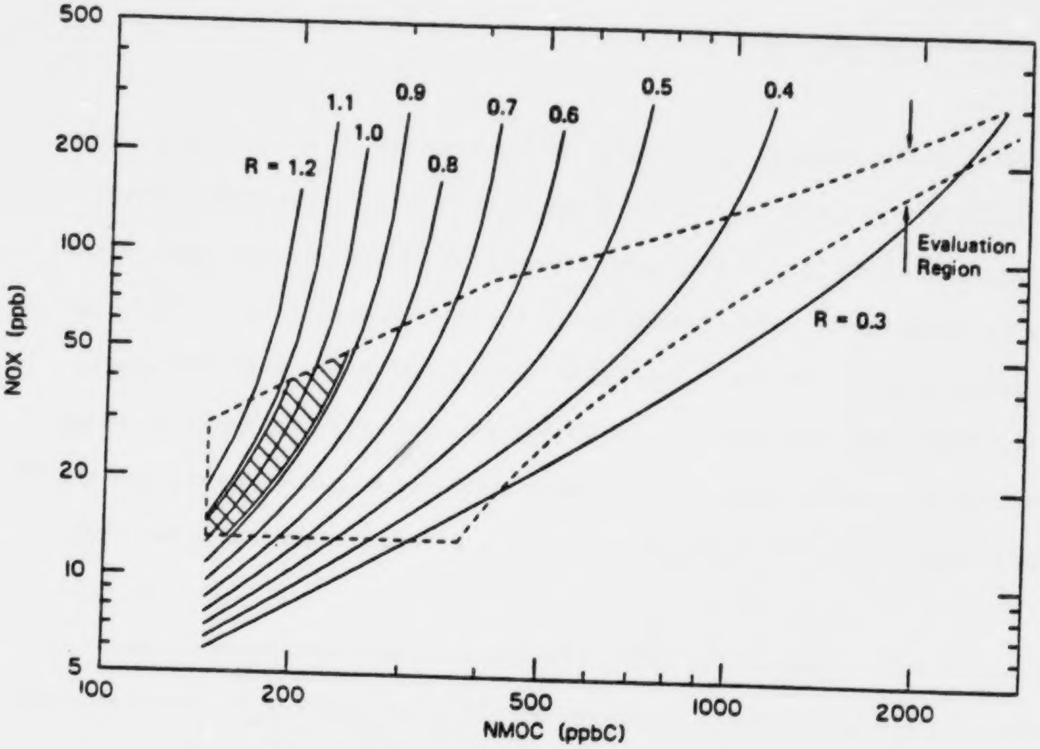
Figure 2-23. Standard-EKMA estimates for DM are similar to CBII predictions.

only one data point in the underpredicted accuracy region (Region 1). In contrast, the Dodge model had five data points in Region 1.

TABLE 2-1. NUMBER OF STANDARD-EKMA O_3 ESTIMATES IN EACH ACCURACY REGION

Model	Accuracy Region		
	Region 1 ($R > 1.2$)	Region 2 ($0.8 \leq R \leq 1.2$)	Region 3 ($R < 0.8$)
Dodge	5	17	78
CBII	1	7	92
DM	1	3	96

Figure 2-24 shows the equation derived for R = REF/EST and the constant-R contours on the NMOC-NO_x plane for the CBII EKMA. Similar to the Dodge EKMA (Figure 2-5), most of the NMOC, NO_x combinations in the evaluation region are expected to overpredict the reference O_3. Accurate estimates of the reference O_3 occur with a relatively small group of NMOC, NO_x combinations depicted by the shaded area in the figure. The shaded area for the CBII model is about 1/3 the size of the shaded area for the Dodge model (Figure 2-5), and the range of NMOC values that will result in an accurate prediction (150 ppbC to 250 ppbC) is also about 1/3 the size of that for the Dodge model (200 ppbC to 500 ppbC). The range of NO_x concentrations resulting in an accurate prediction is not much different for the CBII model (14 ppb to 50 ppb) as for the Dodge model (18 ppb to 50 ppb). The area within the evaluation region where the CBII model is expected to underpredict ($R > 1.2$) is very small.



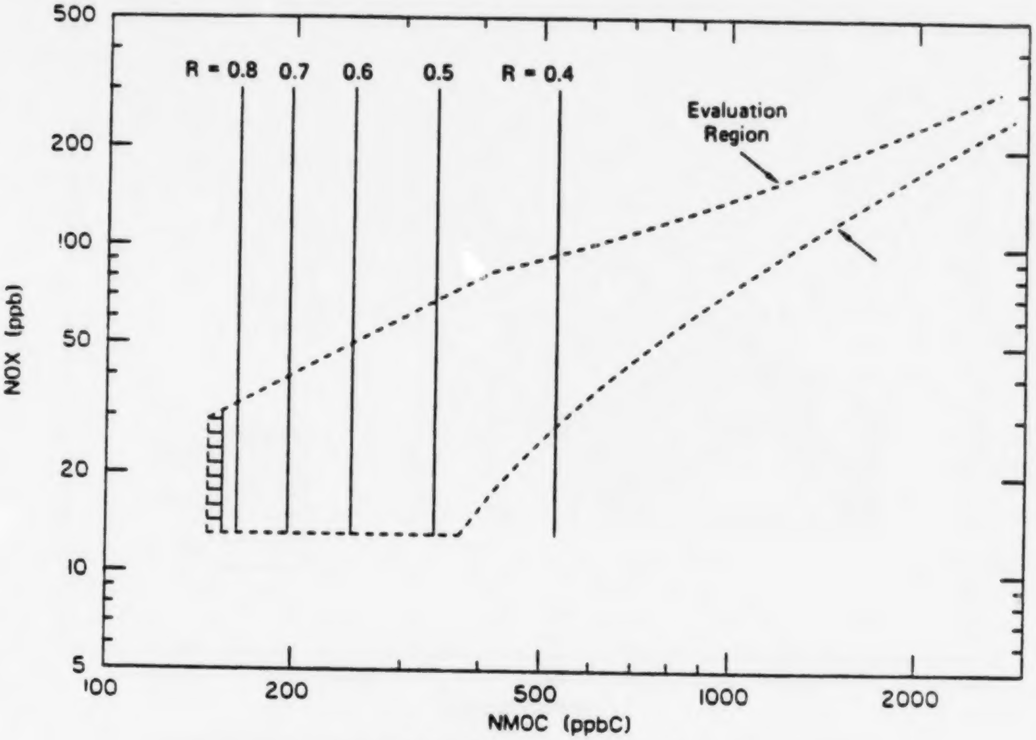
$$R = -0.6 + 200.2/NMOC - 7.8/NO_x + 0.02\ T + 0.004\ BO_3$$

Figure 2-24. CBII/standard-EKMA estimates have a small high-accuracy region compared to the Dodge model's.

Figure 2-25 shows constant-R contours on the NMOC-NO_x plane for the DM EKMA. For the DM model, there are very few combinations of NMOC, NO_x concentrations for which the model is not expected to overpredict the refernce O_3 concentration. There are no NMOC, NO_x combinations for which the DM EKMA is expected to underpredict ($R > 1.0$).

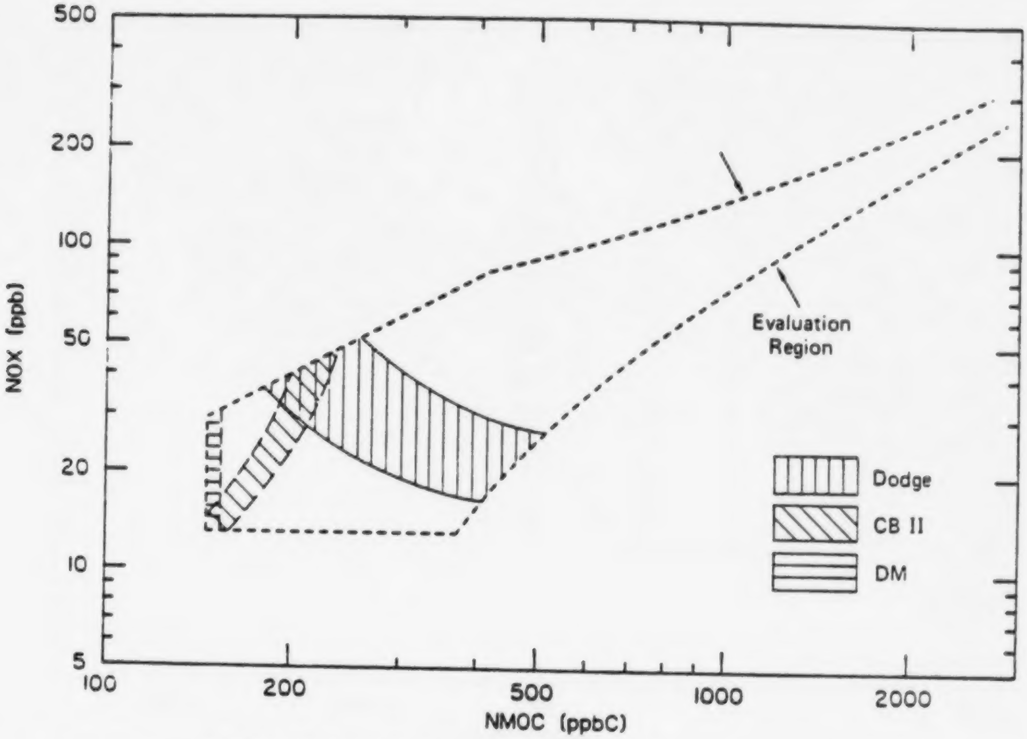
Figure 2-26 compares the regions of the NMOC-NO_x plane for which the probability $P(0.8 \leq R \leq 1.2)$ is at least 0.70 for the three EKMA models. There is little overlap of the areas for the three models, and none of the models is expected to predict accurately for NMOC concentrations > 500 ppb or NO_x concentrations > 50 ppb. The Dodge model is accurate over the widest range of NMOC, NO_x combinations, while the DM model has the smallest range. Figure 2-26 also shows that for low input NMOC and NO_x concentrations, the DM and CBII EKMA models are expected to be more accurate than the Dodge EKMA.

Figure 2-27 compares the CBII city-specific EKMA estimates to the reference O_3 concentrations. Compared with Figure 2-22 for the CBII standard EKMA, we see an increase in the number of points in Regions 1 and 2, and a corresponding decrease in Region 3. However, the majority of the points are still in Region 3. The correlation coefficient between the CBII city-specific EKMA estimates and reference O_3 concentrations is $r = 0.530$. This value is slightly better than the correlation ($r = 0.480$) between the CBII standard-EKMA estimates and the reference O_3 concentrations (Figure 2-22).



$$R = -0.4 + 94.0/NMOC + 0.01\ T + 0.003\ BO_3$$

Figure 2-25. DM/standard EKMA overpredicts over most of evaluation region.



PROB (0.8 ≤ R ≤ 1.2) ≥ 0.7 FOR STANDARD EKMA

Figure 2-26. Accuracy regions for the three models are very different.

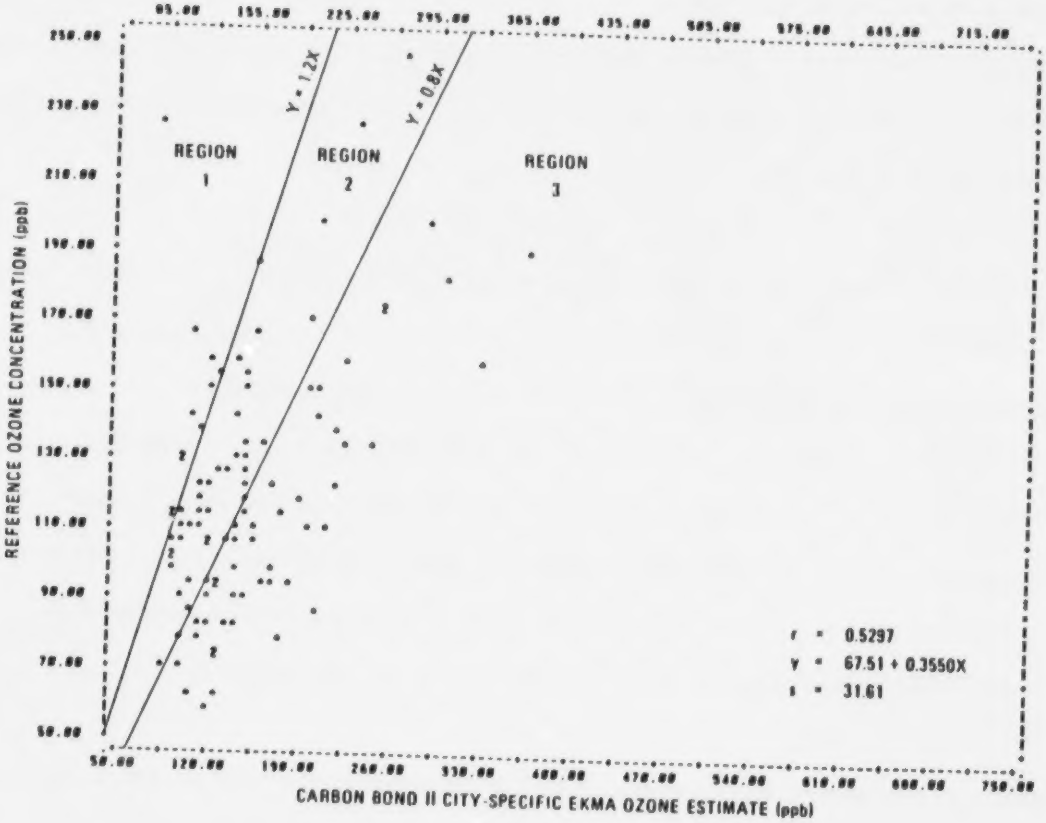


Figure 2-27. CBII/city-specific EKMA estimates have improved accuracy.

Figure 2-28 shows that for the DM EKMA there is no large increase in the number of points in Regions 1 and 2 for the DM city-specific EKMA estimates. However, Figure 2-28, for the DM city-specific EKMA, shows that the scatter in the data is not as widespread as in Figure 2-23 for the DM standard EKMA. The decrease in the overall scatter for the DM city-specific model is indicated by a slightly larger correlation coefficient ($r = 0.480$) as compared with the DM standard EKMA ($r = 0.432$).

Table 2-2 lists the number of cases for each EKMA version for which the city-specific estimates fall within each of the three accuracy regions. Comparing Table 2-2 with Table 2-1 shows a marked improvement in the number of O_3 estimates in Region 2 when changing from the standard to city-specific mode for the Dodge and CBII models. However, the DM model showed only slight improvement. Table 2-1 also shows that the number of O_3 estimates in Region 1 increased for the Dodge and CBII models when changing from the standard to city-specific modes; but for the DM model there was no change.

TABLE 2-2. NUMBER OF CITY-SPECIFIC EKMA O_3 ESTIMATES IN EACH ACCURACY REGION

Model	Accuracy Region		
	Region 1 ($R > 1.2$)	Region 2 ($0.8 \leq R \leq 1.2$)	Region 3 ($R < 0.8$)
Dodge	9	39	52
CBII	10	37	53
DM	1	8	91

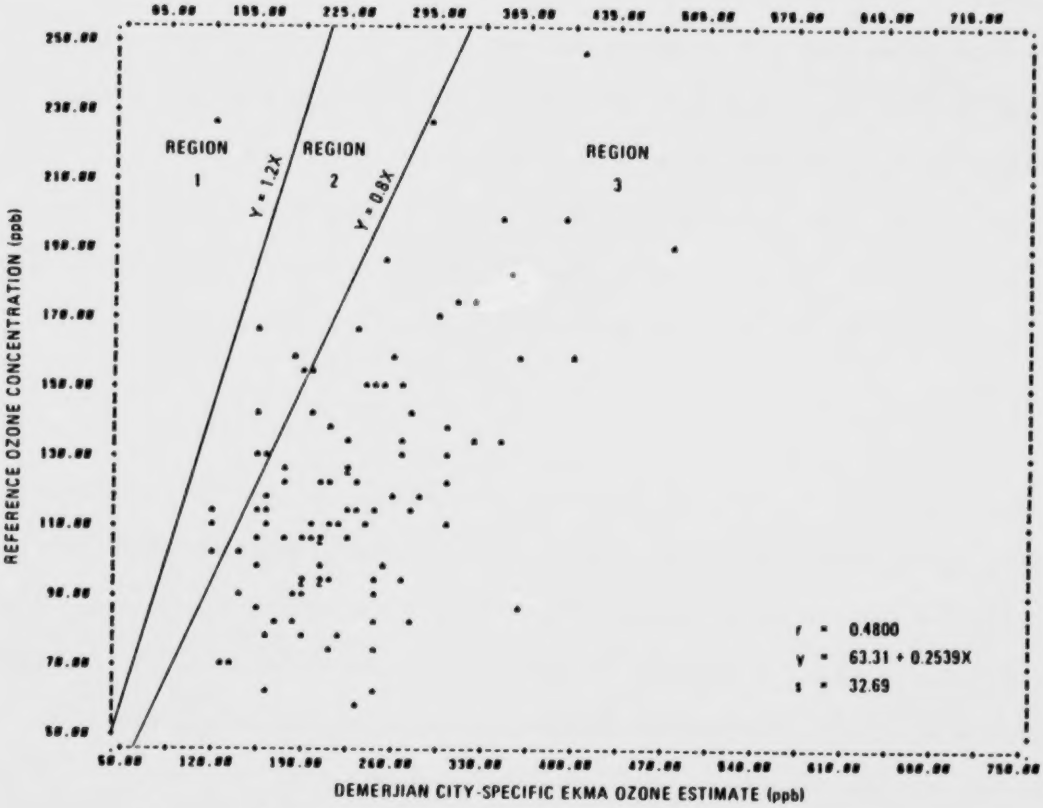


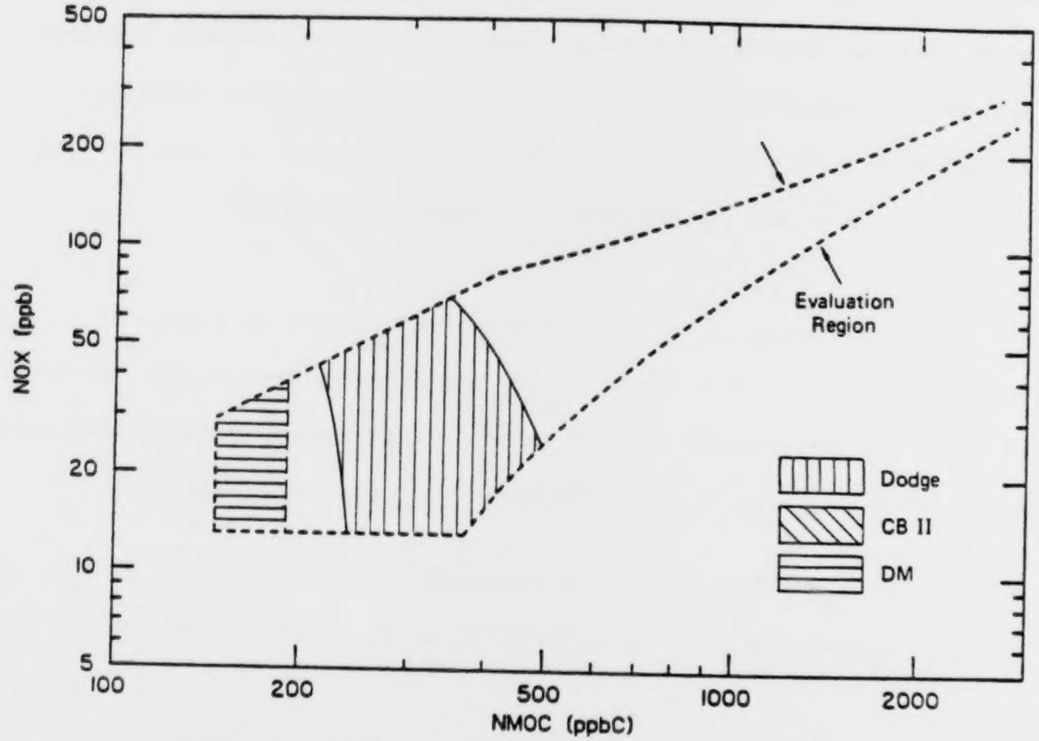
Figure 2-28. Accuracy of DM/city-specific EKMA estimates shows slight improvement.

Figure 2-29 compares the location of the accuracy regions for the Dodge and DM mechanisms in the city-specific mode. The shaded areas correspond to the probability $P(0.8 \leq R \leq 1.2)$ being 70% or greater, that is, where the city-specific estimates have the highest probability of being accurate. Figure 2-29 shows that the areas for the two models do not overlap, and for very low NMOC and NO_x concentrations, the DM city-specific EKMA may predict the reference O_3 concentration more accurately than the Dodge model. Comparing Figure 2-29 with Figure 2-26 for the standard-EKMA models, we see that the areas are larger for the Dodge and DM city-specific models. However, for the majority of NMOC-NO_x paired concentrations, the models still tend to overpredict.

The evaluation showed that the three chemical mechanisms have different accuracy characteristics. Thus, the accuracy regions of the NMOC-NO_x plane are different for the three models. This feature suggests the following criterion for choosing a chemical mechanism for a particular EKMA application: select the model with the highest probability of producing an accurate prediction for the specific application of interest.

EKMA APPLICATIONS

Using EKMA to estimate maximum O_3 from its NMOC and NO_x precursors implies that EKMA could be used to assess the effect on O_3 of actions that modify the concentration of NMOC and NO_x, for example, emissions control strategies. A corollary is that EKMA could also be used in the design of



PROB (0.8 ≤ R ≤ 1.2) ≥ 0.7 FOR CITY-SPECIFIC EKMA

Figure 2-29. Regions where accurate estimates are at least 70% probable do not overlap.

control strategies by performing a sequence of analyses of the effect on O_3 of a variety of postulated control measures. Below we examine the possibilities and pitfalls of using EKMA in this fashion in light of the results of this study. The discussion will be cast in terms of emissions control strategies, because we consider this to be the most common application of EKMA. However, it should be understood that any action that modifies precursor levels is implicitly treated. The discussion assumes that the reader is familiar with the principles and assumptions of EKMA as presently formulated.

The problem at issue is to evaluate the effectiveness of a control strategy aimed at reducing O_3 by curtailing emissions of NMOC or NO_x, or both. In this context, EKMA could be used to estimate the maximum O_3 associated with the control strategy in an attempt to answer the following questions:

- What is the probability that the maximum O_3 will exceed 120 ppb?
- If it appears that 120 ppb will be exceeded, is the estimated O_3 close to or much greater than 120 ppb?

One general procedure, which we call the point-estimate method, is depicted in the flow chart in Figure 2-30. EKMA could be used to answer the first question provided that the O_3 estimate is less than or equal to 120 ppb, and there is a high probability that the estimate is an upper bound for the actual concentration. This corresponds to taking the right-hand branch of Figure 2-30. In this case, the answer to Question 1 above is that the probability that the control strategy will produce O_3 levels that exceed 120 ppb is very low; the precise value of the probability would be obtained from

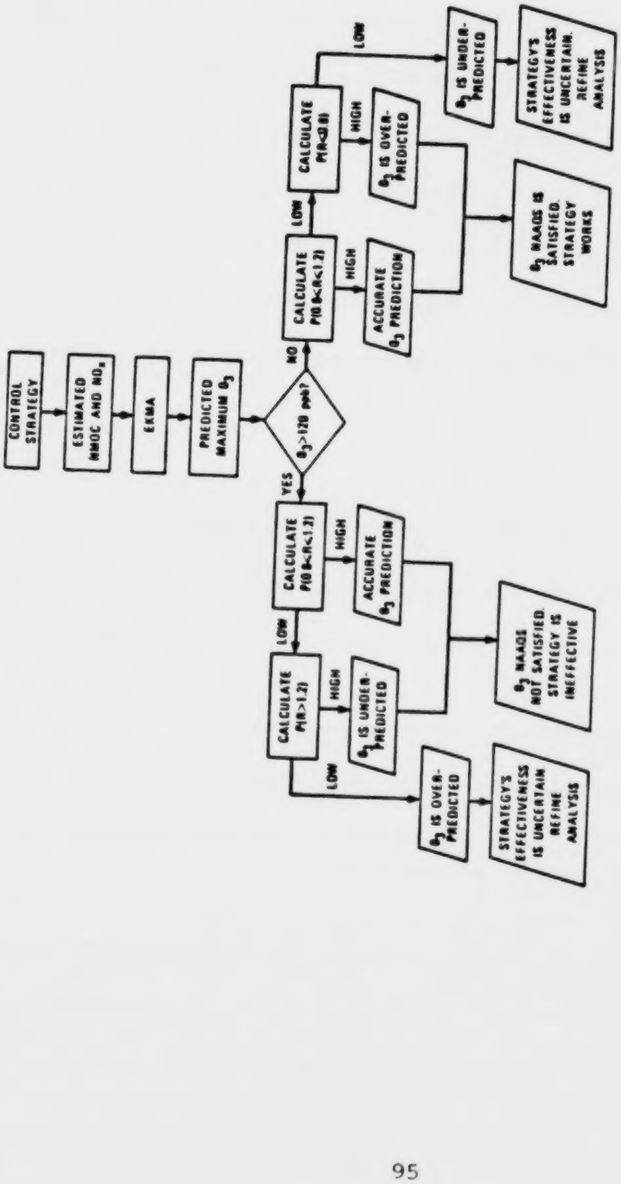

CONTROL STRATEGY
ESTIMATED NMOC AND NO_x
EKMA
PREDICTED MAXIMUM O_3
O_3>120 ppb?
YES
NO
CALCULATE P(0.8<R<1.2)
HIGH
LOW
ACCURATE O_3 PREDICTION
CALCULATE P(R>1.2)
HIGH
LOW
O_3 IS UNDER-PREDICTED
O_3 IS OVER-PREDICTED
O_3 NAAQS NOT SATISFIED. STRATEGY IS INEFFECTIVE
STRATEGY'S EFFECTIVENESS IS UNCERTAIN REFINE ANALYSIS
CALCULATE P(0.8<R<1.2)
HIGH
LOW
ACCURATE O_3 PREDICTION
CALCULATE P(R<0.8)
HIGH
LOW
O_3 IS OVER-PREDICTED
O_3 IS UNDER-PREDICTED
O_3 NAAQS IS SATISFIED. STRATEGY WORKS
STRATEGY'S EFFECTIVENESS IS UNCERTAIN. REFINE ANALYSIS

Figure 2-30. Point-estimate method.

accuracy probability plots such as Figure 2-4. Note that the accuracy of the O_3 estimate is not important in this situation because an upper-bound estimate is all that is needed. Hence, standard EKMA may be satisfactory for this application.

EKMA would not be as helpful in answering Question 1 if the estimate is under 120 ppb, but there is a high probability of underprediction. As indicated in the right-most branch of Figure 2-30, in this case, the analysis must be refined to establish the accuracy of the estimate and the probability associated with that accuracy. The methods previously described allow a user to perform such a refined analysis. Because accuracy is important in these circumstances, it may be necessary to resort to city-specific EKMA to obtain the O_3 estimate.

Answering Question 2 requires analyzing the accuracy of the estimate and its associated probability. As depicted in the left branch of Figure 2-30, three cases are to be considered when the estimate is over 120 ppb:

- There is a high probability of overprediction.
- There is a high probability of underprediction.
- There is a relatively high probability that the estimate is accurate, for example, to within ± 20%.

EKMA would be least helpful in the first case (the left-most branch of Figure 2-30), because although the control strategy may actually reduce O_3 below 120 ppb, the overprediction masks the effect. This case thus requires a very thorough analysis of the accuracy of the estimate. In the second case, the control strategy clearly does not work, and the margin of ineffectiveness should be assessed by analyzing the accuracy of the estimate as a means of guiding the reformulation of the control strategy. The third case is where EKMA would be most useful, because the estimate is relatively accurate. Such an estimate can also be used to guide the design of a new control strategy.

Used in the fashion described above, EKMA can be considered as a screening tool, albeit coarse at times, that allows one to analyze the potential impact of a control strategy. Coupled with the analysis of the accuracy of the estimates, EKMA could also be used to help formulate a control strategy by sequentially screening a series of control strategies. In general, we recommend applying standard EKMA first, then going to the city-specific mode if the results obtained with the standard mode warrant it.

The screening model provided by the point-estimate method is of the go/no-go type, and is based on a single O_3 prediction. The Monte Carlo method, by contrast, is designed to predict the distribution of O_3 maxima, from which one can estimate the statistical information required by the O_3 air quality standard. Figure 2-31 shows a flowchart of the Monte Carlo method. The input consists of N pairs of NMOC and NO_x concentrations drawn from a joint distribution; N is an arbitrary number determined by statistical criteria. The NMOC, NO_x distribution is associated with a postulated control strategy. For example, one could obtain a joint distribution of NMOC and NO_x by scaling an observed distribution. The N pairs of NMOC and NO_x are used

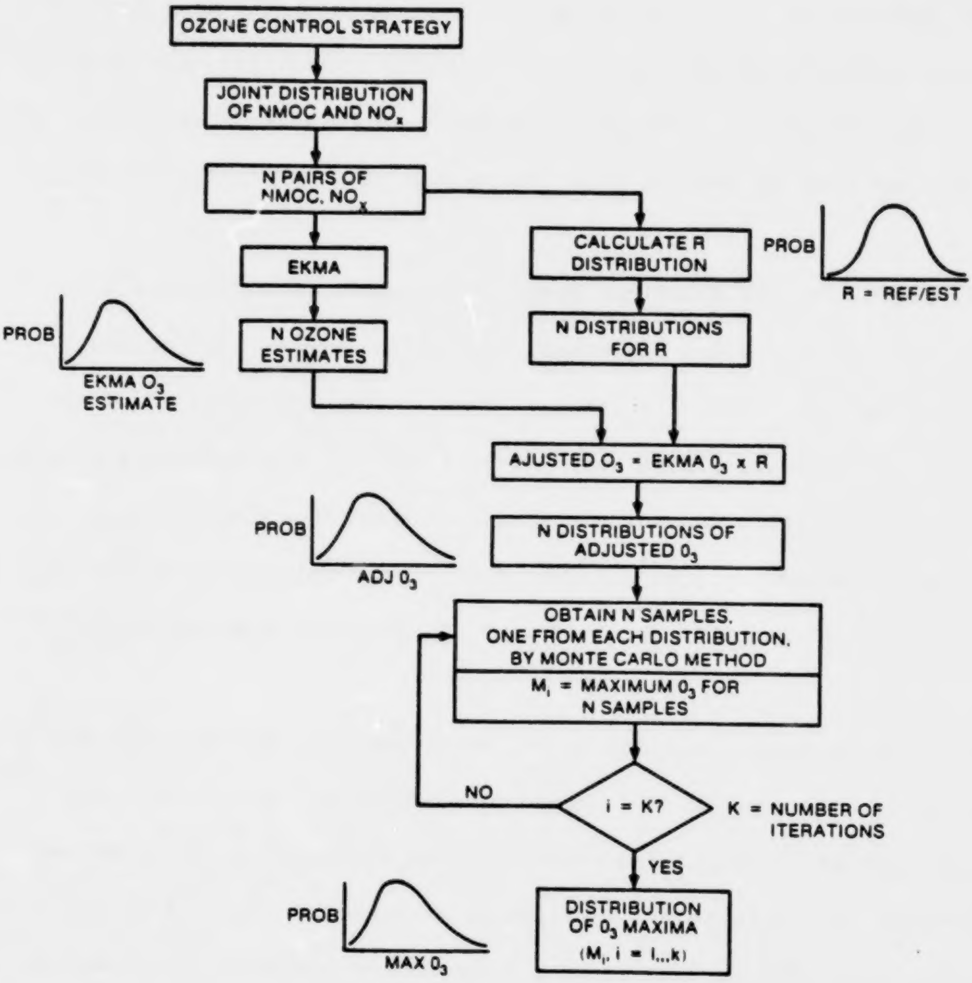

OZONE CONTROL STRATEGY
JOINT DISTRIBUTION OF NMOC AND NO_x
N PAIRS OF NMOC, NO_x
EKMA
N OZONE ESTIMATES
PROB
EKMA O_3 ESTIMATE
CALCULATE R DISTRIBUTION
PROB
R = REF/EST
N DISTRIBUTIONS FOR R
AJUSTED O_3 = EKMA O_3 x R
PROB
ADJ O_3
N DISTRIBUTIONS OF ADJUSTED O_3
OBTAIN N SAMPLES, ONE FROM EACH DISTRIBUTION, BY MONTE CARLO METHOD
M_i = MAXIMUM O_3 FOR N SAMPLES
NO
i = K?
K = NUMBER OF ITERATIONS
YES
PROB
MAX O_3
DISTRIBUTION OF O_3 MAXIMA (M_i, i = 1...k)

Figure 2-31. Monte Carlo method.

with EKMA to obtain N O_3 estimates. Each NMOC, NO_x also defines a distribution of the ratio R = reference O_3/estimated O_3. The next step is a key element of the method: we obtain an adjusted O_3 estimate by multiplying the EKMA O_3 estimate by its corresponding R distribution. Thus, in this step we compensate for the expected error in the EKMA estimate. In this manner we obtain N distributions of adjusted O_3 estimates. As Figure 2-31 indicates, we then obtain a distribution of O_3 maxima by using Monte Carlo sampling with the N distributions of adjusted O_3 estimates.

The Monte Carlo method has several advantages:

- It uses the entire distribution of NMOC and NO_x. This contrasts with the conventional approach to the use of EKMA, which uses only the median of the distribution of NMOC:NO_x ratios.
- It compensates for modeling errors. The error structure of EKMA is reflected in the distribution of R, and this distribution is used to adjust the EKMA estimates.
- It estimates the distribution of O_3 maxima, which provides the statistics required by the O_3 air quality standard.

Both the Monte Carlo and point-estimate methods can be used as screening tools for statistically analyzing the effectiveness of a control strategy. Such a statistical approach is consistent with the O_3 air quality standard, which is itself statistical.

To apply EKMA in the manner described, one must have a means of calculating the accuracy, and its associated probability, of the O_3 estimate. This, of course, presumes that EKMA performance has been already evaluated following the methods described in this report. Hence one would have available probability curves and equations for the R ratio, such as shown in Figure 2-4, for analyzing the accuracy of the emissions.

ACKNOWLEDGMENT

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WORKSHOP COMMENTARY

DIMITRIADES: How did you deal with the variation in sunlight intensity from day to day? Did you screen out all the data for cloudy days?

MARTINEZ: No. We were interested in predicting the maximum potential O_3 for an area. So we fixed the meteorological variables. In essence, we had one set of meteorological conditions for all the points I showed you. The only things that changed were the HC and the NO_x.

We fixed the meteorological variables, based on the data analysis. Like standard EKMA, it has fixed meteorology, but the meteorology is tailored for a city in the city-specific case, and based on the data analysis.

DIMITRIADES: Let me see if I understand. When you say that in those points EKMA overpredicts, couldn't that be because during those days the sunlight intensity was low and that's why we had an overprediction?

MARTINEZ: It's possible. The wind may have been 40 mph. There are a number of reasons for that.

DIMITRIADES: Well, you're not just saying that the EKMA model is bad?

MARTINEZ: No, in fact, I consider overpredictions very useful because they give you the upper bounds that can help you in the go/no-go type screening.

Underpredictions are more worrisome to me.

Basically, I wanted to characterize the errors of EKMA used in this way. When I say that EKMA overpredicts, I'm not saying that it is bad.

ESCHENROEDER: I have a couple of questions, Dr. Martinez, which probably indicate that I don't really understand the Monte Carlo method.

One question is how do you enter the method and get your joint distribution of HC or NMOC and NO_x points, if it is for some time in the future or some configuration that doesn't--

MARTINEZ: That has nothing to do with the Monte Carlo method. That is an input.

ESCHENROEDER: An input of historical statistics.

MARTINEZ: You can do it several ways. You can, given an O_3 control strategy to control HC'S and NO_x such as Dr. Trijonis discussed here, take an existing distribution and decrease HC, the mean HC, by 20% and the mean NO_x by 15%.

You also have to consider the correlation between the two. Then, if you want to, you can keep the same variance as the existing distribution and change that everywhere, then use that as your base distribution.

Alternatively, you can try to come up with an emissions model that can give you sources and that can relate the sources to the concentrations of HC and NO_x. That is simpler than estimating O_3 from the emissions themselves.

ESCHENROEDER: So you are saying that you don't need to know what the joint frequency distribution of these might be in the future. You just take a point and then find out what the probability of your O_3 prediction is as far as the correctness of over or underpredicting?

MARTINEZ: You have to postulate a joint probability distribution for the HC and NO_x.

ESCHENROEDER: You do have to know that then?

MARTINEZ: Yes.

ESCHENROEDER: Okay. I think that is the problem.

MARTINEZ: It could be just a set of points. You don't have to say that it is a Gaussian or a log normal distribution or whatever. Just a set of points will do it.

ESCHENROEDER: I'm thinking of the user, who having read this in the Federal Register, says that it's hard enough to just take existing data, not to mention an estimated joint frequency distribution of NMOC.

MARTINEZ: I think, looking at this from California, we haven't really--

ESCHENROEDER: I'm trying to think what step--

MARTINEZ: --handholding with the potential user, but that is a necessary step, no question.

ESCHENROEDER: The second question is, does the Monte Carlo approach actually constitute a rational method of correcting EKMA? In other words, are you considering what, when there is an overprediction, you're going to modify?

MARTINEZ: Yes, provided, of course, that you have good statistics for your EKMA errors and for your distribution of what the ratio is. It certainly compensates for modeling errors.

ESCHENROEDER: Is there any other rational method for correction? In other words, given that the patterns are similar from city to city and model to model, is there some simple, rational correction scheme for EKMA that might have occurred to you in doing this?

MARTINEZ: I would have to look into that. That would be an extension of the present work. This is fairly new.

ESCHENROEDER: I would encourage that because it looks like there may be some way of fixing the patterns.

MARTINEZ: Yes, undoubtedly.

ESCHENROEDER: Purely empirical.

MARTINEZ: There are a lot of things behind this that I haven't mentioned, for lack of time. One is that the city-specific EKMA and standard EKMA predictions were all very highly correlated, and I mean 0.98 and 0.99.

It seems like one should be able to derive one from the other and then go with only one of them. It may be that standard EKMA is the one to choose. That should be investigated.

McRAE: Dr. Martinez, I would like to follow up on a question that Dr. Dimitriades raised with regard to the choice of the meteorological conditions. How did you go about choosing those meteorological conditions that would produce the maximum O_3 in the region?

Related to that question, if you put in the specific meteorology of the day, wouldn't that, using city-specific EKMA, tend to tighten up the accuracy bounds on the predictions?

MARTINEZ: Well, no.

Concerning the first question, we examined the data bases for all these places, and our concern was to come up with meteorological conditions that were associated with high O_3. The data that went into the model were those obtained on the date when the highest O_3 occurred. We felt that on that day there was enough sunlight.

Concerning the second question, the NO_2/NO_x ratio was the average of the ratios for the 5 days with the highest O_3.

The background O_3 was the same for the cases that we have information on. Background O_3 was the average of the 5 days of the highest observed O_3 concentrations.

We used wind speeds and wind trajectories to come up with post-8:00 a.m. emissions.

We took the emissions inventory for the areas in question, we plotted the emissions on a map, and then we drew a set of circles based on the central region, and computed emissions densities along trajectories.

The trajectories were based on several days, at 5 days or so, on which the highest O_3 concentration values were observed, so you have fairly low wind speeds for those days.

We averaged the trajectories out and came up with the amount of the increments of the emissions after 8:00 a.m..

So if you have a slow trajectory, it means lots of emissions for a while after 8:00 a.m.. If the winds are high, then, of course, you don't have as much emissions input.

McRAE: The second question was, why wouldn't you tighten up the error bounds if you used better characterization of the physical processes?

MARTINEZ: Could you rephrase the question?

LLOYD: If you put in the specific meteorology for those 5 days, since you are putting more physics into the problem, I would expect that you would--

MARTINEZ: We have data for a lot of other days in there that have somewhat different meteorology, and that meteorology is reflected in the ambient concentrations of HC and NO_x. So, it probably washes out.

LLOYD: Did you check the chemical mechanism against any other data base besides the St. Louis one?

MARTINEZ: No. But I'm going to check it against the Houston data base.

UNIDENTIFIED SPEAKER: In the State Implementation Plan (SIP) guidelines for the application of the EKMA model, we request the states and local agencies to use day-specific meteorological inputs for each day that they model, and, indeed, we have found that the results obtained with the model are pretty dependent on these day-specific meteorological inputs.

I think that has also been found to be the case when mechanisms other than Dodge's have been incorporated into the model.

One of the interesting observations you had, however, was that when you switched from standard inputs to city-specific inputs, not all of the mechanisms reacted to that in exactly the same way.

For example, there was a difference between Carbon Bond II and the Demerjian mechanisms in St. Louis, and I suspect that is a topic that we will probably be discussing tomorrow.

MARTINEZ: I have a lot of other things that I could tell you about that. First of all, the Demerjian mechanism behaved very differently in many, many respects.

For one thing, if you plot the relative change in the O_3, going from the standard to a city-specific EKMA model, there is a function of the input HC. It's essentially over 25% for all the hundreds of points.

Regardless of what the value for the O_3 concentration was, you got a horizontal line. There appears to be a saturation here. No matter what you do to that model, it reduces everything by 25%. That's very strange.

Another thing is that for the predictions of the Dodge and Carbon Bond II models where linearly correlated, and generally highly linearly correlated, the predictions of the Demerjian model and the other two were correlated in a nonlinear fashion.

In fact, the parabolic curve is quite noticeable. You can fit a nice parabola to that, and the correlation then becomes very high. The Demerjian model does things in a different way compared to the other two.

DUNKER: When you go to these other mechanisms, they have different HC species. Particularly, the Carbon Bond mechanism uses the ethylene aromatics. Have you changed the HC mix for those tests?

MARTINEZ: Yes, Dr. Jeffries has. Based on his work with the EKMA model, he was able to translate the HC, overall HC-NMOC concentration into different species.

DUNKER: But aren't you then comparing not simply different mechanisms, but possibly different HC reactivities?

MARTINEZ: That is possible.

DUNKER: You are comparing it in terms of absolute O_3 with observed ambient data. I think that would be important.

MARTINEZ: It's possible that that is the case. The only thing that we know for sure is that the different HC species in the Demerjian model add up to the same number as the ones in the Carbon Bond II model. But, their speciation is somewhat different.

Dr. Jeffries, would you like to address that point?

JEFFRIES: I'll talk a little bit more about that tomorrow when I give my presentation on the mechanisms in St. Louis.

For the St. Louis work, we took the emissions inventory values that had been used for the 10 days that Dr. Whitten is going to talk about and I will speak about briefly tomorrow.

All the mechanisms had the same composition, but each mechanism, of course, has its own rules for how you take a particular composition and input it into the mechanism. Each mechanism has its own set of carbon numbers, its own set of average molecular weights. The Carbon Bond II has a different treatment than the Demerjian mechanism, and to the extent possible, we took into account all those factors in putting them in.

I'll show comparisons of the mechanisms against Demerjian's tomorrow.

DUNKER: I guess I'm saying that you can run, for example, the Carbon Bond II mechanism with the same butane/propene mix.

JEFFRIES: That was not done. The effort was not to make Carbon Bond II simulate Dodge's mechanism; the effort was to make Carbon Bond II simulate the St. Louis data.

DUNKER: Right, but I think there are two questions here. One is the difference in chemical mechanisms, and possibly rate constants and half weights. The second question is the difference in HC reactivities as you go from the EKMA mechanism, which has a limited number of HC species, to some of these other mechanisms where you can have other species in there like ethylene or aromatics.

When you're comparing, you can change then to another mechanism. When you put in something more realistic in terms of the inventory, it's not surprising that you might get different O_3 values.

MARTINEZ: That's the object.

DIMITRIADES: We will be discussing this tomorrow, the mechanisms.

WHITTEN: Dr. Martinez, I am troubled by the whole basic approach that you've taken here.

My understanding of EKMA is that it is a model where the meteorology is held completely fixed and only the emissions, the concentrations, and the chemistry are allowed to vary on different points of the diagram. So I am troubled that you've taken different HC and NO_x concentrations, which, to my mind, are not changing because of the emissions. Emissions from day to day are usually quite constant.

MARTINEZ: That's not true.

WHITTEN: The difference in the HC and NO_x concentrations that you see in the atmosphere is due primarily to the differences in meteorology and micrometeorology from day to day. You might have poor mixing in the morning and get a pocket of HC one day that doesn't come down that same street the next day, even though the meteorology, generally, is somewhat the same. So you see large fluctuations in HC and NO_x concentrations, but these fluctuations are not the same kind of fluctuations that the model is intended to take into account.

These are meteorological fluctuations, not emissions fluctuations.

MARTINEZ: I disagree on several counts. First of all, when you say that the meteorology is held fixed on a diagram produced, how do you think that when you produce a diagram you have to change HC and NO_x to--

WHITTEN: That's all that's changed.

MARTINEZ: But, in reality, how does that change, in--

WHITTEN: But the model is designed to have fixed meteorology on every single point of that diagram. The only thing that changes--

MARTINEZ: All I'm doing is changing the HC and the NO_x, except that I'm using atmospheric measurements of HC and NO_x and you're estimating HC and NO_x.

WHITTEN: I think there are fluctuations due to instrument calibration, micrometeorology, and other meteorology. These are not fluctuations in emissions that you're looking at.

I think that you're not really testing the model. You're testing something else.

MARTINEZ: I'm testing it in a different way.

TRIJONIS: I have studied this problem in Los Angeles. I have to agree with Dr. Whitten that there is definitely a correlation between meteorology and the morning HC/NO_x ratio.

Low ratio days tend to be winter days: high ratio days tend to be summer days. There are also other things. High ratio days tend to be days of greater carryover.

There is a correlation between the meteorology and the ratio.

MARTINEZ: No, if there weren't, we wouldn't have any problems.

It's a different way of looking at EKMA. You can consider EKMA as a transfer function. It's an engineering point of view with which I've approached the model.

I instinctively dislike using, for example, a single ratio, such as a median ratio, to characterize a whole distribution of $NMOC/NO_x$ ratios. That was one point that led me to think along these lines.

The sensitivity to the HC/NO_x ratio has been shown to be very large, which is only to be expected from the shape of the contours and the way the ratio is plotted. Any rather small change in the ratio will give you large changes in the O_3.

To produce an O_3 isopleth diagram, you fix everything except the HC and the NO_x, and then you postulate a lot of HC's and NO_x to give you points on that diagram through which you draw your O_3 isopleths. That is basically the same thing I was doing, except that I didn't draw any isopleths, and instead of postulating HC's and NO_x, I used measured HC and NO_x.

[AUTHOR'S NOTE: Upon further reflection, I agree with Dr. McRae that it may be possible to obtain smaller error bounds for the predictions by using day-specific meteorology.

3. PREDICTING OZONE FREQUENCY DISTRIBUTIONS FROM OZONE ISOPLETH DIAGRAMS AND AIR QUALITY DATA

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ABSTRACT

Air quality data are used to derive an ozone isopleth surface that predicts the observed ozone frequency distribution from the observed joint distributions of hydrocarbons and oxides of nitrogen. The method uses a seven-parameter mathematical description of the ozone isopleth surfaces. The process begins with parameter values that describe the standard Dodge chemistry EKMA surface or a standard carbon-bond chemistry EKMA surface, and uses a nonlinear convergence technique to find the parameters for a specific city. Once a surface is found, the precursor distributions can be modified and the surface used to predict the new ozone distribution. The method has been applied to St. Louis, MO Regional Air Pollution Study data.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has suggested four levels of ozone (O_3) modeling analysis that could be applied to urban areas (Federal Register, 1979). These are photochemical dispersion models, simplified trajectory models, the standard Empirical Kinetic Modeling Approach (EKMA), and city-specific EKMA. The last three are based on the concept of generating a maximum O_3 surface as a function of initial nonmethane hydrocarbon (NMHC) and oxides of nitrogen (NO_x) concentrations. A particular surface is created by performing simulations with a photochemical mechanism under a fixed set of meteorological conditions together with fixed emissions characteristics and boundary conditions.

Although each of the assumptions used in choosing the O_3 surface can be justified on the basis of available knowledge or expediency, taken together they do not seem to constitute a solid foundation on which to build control strategies. Jeffries et al. (1981) showed that different sets of assumptions, all justifiable, led to O_3 surfaces which for a given scenario (in St. Louis) required hydrocarbon (HC) controls that varied from 15 to 80%. The two most significant factors in this variation were in the choice of a representation of meteorological conditions for a particular day and in the choice of a photochemical mechanism.

Despite the difficulties inherent in these simple modeling analyses, they have been pursued on the hypothesis that when model predictions are not in agreement with observations, a procedure (EKMA) is available to correct the application of the O_3 surface to ambient conditions, and control strategies can then be evaluated. Jeffries et al. (1981) showed, however, that this technique can produce results in which the degree of control calculated is correlated with the degree of absolute prediction of the maximum O_3 in the base case.

An alternative approach, first introduced by Post (1979), is to determine an O_3 surface that relates the observed distribution of precursor concentrations with the observed distribution of maximum O_3 concentrations. That is, an O_3 isopleth diagram is used not to predict the concentration of O_3 from the concentration of precursors, but to predict the relative frequency of occurrence of O_3 concentrations. Such a surface does not imply a single set of meteorological conditions, but embodies a probability distribution of conditions specific to the period and location of the data collection. It does not attempt to predict the maximum O_3 concentration measured on a particular day, but rather the surface, together with the precursor distribution, represents a statistical transformation of the precursors into measured O_3. That such a surface might exist was suggested by the work of Post (1979). Holton and Jeffries (1979) found an easy method for manipulating the surfaces.

As part of the Sydney Oxidant Study, Post (1979) had obtained HC, NO_x, and O_3 data along 16 trajectories. When the initial HC and NO_x concentrations were plotted on a standard Dodge isopleth diagram, Post observed that if the

O_3 values of the isopleth lines were multiplied by 0.6, then the diagram would be nearly absolute. Further, when the more than 800 half-hourly averaged pairs of NMHC and NO_x from 6 to 10 a.m. were plotted on this scaled diagram, the relative frequencies of predicted O_3 concentrations agreed well with the observed frequencies of O_3 obtained by the five-station O_3 monitoring network operated by the State Pollution Control Commission.

Holton and Jeffries (1979) noted a relatively simple mathematical formulation for maximum O_3 surfaces as functions of precursor concentrations. This formulation is based on a rotation of the HC and NO_x axes through an angle $(90-\theta)$, where θ is the angle between the ridge line and the NMHC axis. The ridge line is that line through the points on each isopleth representing the minimum sum of [NMHC] and $[NO_x]$. If the new axes are called D and L, where D is positive to the right of the ridge line and L is positive along the ridge line (Figure 3-1), then

$$L = [\mathrm{NMHC}]\cos\theta + [NO_x]\sin\theta \qquad (3\text{-}1)$$

$$D = [\mathrm{NMHC}]\sin\theta + [NO_x]\cos\theta \qquad (3\text{-}2)$$

Holton and Jeffries (1979) found that for concentrations less than about 2 ppm the ridge line points lie on a straight line. They also found that an adequate representation of a particular O_3 surface was a power function of the form:

$$[O_3] = cL^n \qquad (3\text{-}3)$$

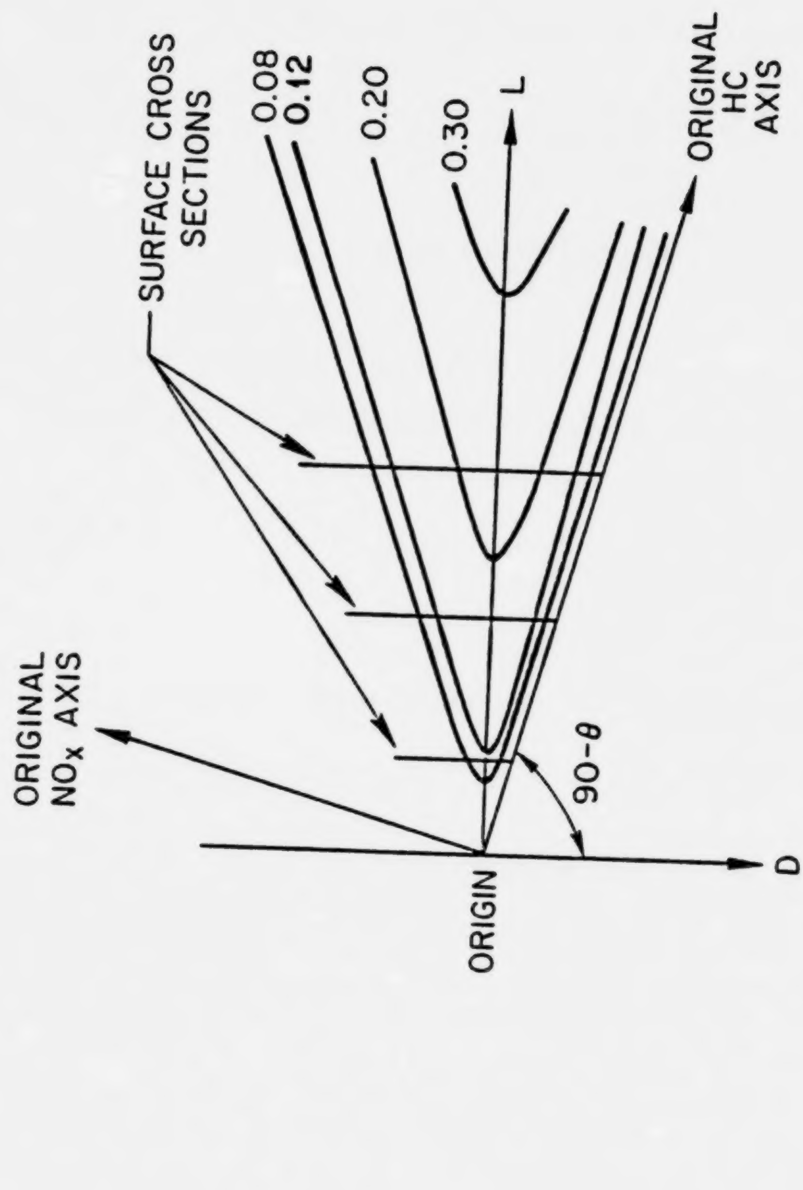

ORIGINAL
NO_x AXIS
ORIGIN
D
90-θ
SURFACE CROSS
SECTIONS
0.08
0.12
0.20
0.30
L
ORIGINAL
HC
AXIS

Figure 3-1. Projection of an O_3-precursor surface into the L-D plane showing the (90-θ)° rotation of the original HC and NO_x axes and three surface cross sections.

up the ridge line ($D = 0$), with an elliptic cross-section for $D > 0$ and an exponential cross-section for $D < 0$. Holton (1981) suggested a more general form:

$$[O_3] = cL^n[1 - (D/(L\tan\theta))^g]^h \text{ for } D > 0$$

and

$$[O_3] = cL^n\exp[-q(-D/L)^r] \text{ for } D < 0 \qquad (3\text{-}4)$$

It was decided to extend the work of Post by fitting a surface of the form of Equation (3-4) to the precursor and maximum O_3 concentrations forming part of the St. Louis data base.

GENERAL PROCEDURE

The functional form Fquation (3-4) for the O_3 surface involves seven parameters: c, n, θ, g, h, q, and r. Suppose

$$(H_{ij}, N_{ij}) \; i = 1,..m \text{ sites}, \; j = 1,..n \text{ days}$$

is a set of measured HC and NO_x precursor pairs and that

$$Z_j = \max \{Z_{ij}\} \; i = 1,..m \text{ sites}$$

is the maximum of the measured O_3 concentrations on day j. Then if

$$Z^*_j = \max\{f(H_{ij},N_{ij},c,n,e,g,h,q,r)\} \qquad (3\text{-}5)$$

is the maximum of all the O_3 concentrations predicted by Equation (3-4) for each day, the seven parameters can be chosen so that the frequency distribution of Z^*_j, the predicted values, matches as closely as possible the frequency distribution of Z_j, the measured regional O_3 maximum, over all days $j = 1....n$.

The algorithm used to find the values of the parameters was a modification of the nonlinear least-squares estimation of Marquardt (1963). Rather than minimizing the differences in concentrations on the same day,

$$\sum_{j=1}^{n}[Z^*_j - Z_j]^2, \text{ the value of } \sum_{j=1}^{n}[F_i(Z^*) - F_i(Z)]^2$$

was minimized, where $F_i(Z)$ is the percentage frequency of concentrations in class i, with an interval width of 0.01 ppm O_3 (Table 3-1).

The following iterative procedure was adopted:

(1) Choose initial estimates for the parameters which specify the O_3 surface.

(2) Use this surface to predict a maximum O_3 concentration for each day of the period, given all of the precursor pairs measured during the morning period of that day.

(3) Check the predicted maximum O_3 frequency distribution against the observed distribution.

(4) Modify the parameters and return to step 2.

Because of the large number of precursor pairs involved, it was more efficient to note for each day the particular precursor pair that generated maximum O_3 and to retain that set of pairs through several iterations before returning to the complete precursor set.

It is possible that several different surfaces will generate a maximum O_3 frequency distribution similar to that observed. The assumption was made that the final surface should have a similar shape as those generated by simulations using chemical mechanisms derived from smog chamber studies and kinetics models. For this reason the initial approximation to the St. Louis surface was chosen to be the standard Dodge isopleth surface generated by the default conditions in the Ozone Isopleth Plotting Package (OZIPP) computer program (Figure 3-2). It was, therefore, necessary to select parameter values for the functional form Equation (3-4) which reproduced the Dodge surface. The values that give a close approximation are shown in the first row of Table 3-2. The fitted isopleth surface is shown in Figure 3-3.

TABLE 3-1. PARAMETERS FOR O_3 ISOPLETH SURFACE EQUATION*

Surface	Ridgeline			Right		Left	
	c	n	θ	g	h	q	r
Standard Dodge	0.307	0.657	0.198	1.60	0.500	9.0	1.6
St. Louis Dodge	0.143	0.668	0.192	1.54	0.529	8.78	1.6
CBII (Med React)	0.50	0.640	0.56	1.70	0.56	5.4	1.5
St. Louis CBII	0.140	0.639	0.562	1.70	0.562	5.4	1.5

*$[O_3] = (cL^n)(1-(D/\tan \theta L)^g)^h$ for $D > 0$; $[O_3] = (cL^n) \exp(-q(-D/L)^r)$ for $D < 0$; $L = [NMHC] \cos \theta + [NO_x] \sin \theta$; $D = [NMHC] \sin \theta + [NO_x] \cos \theta$.

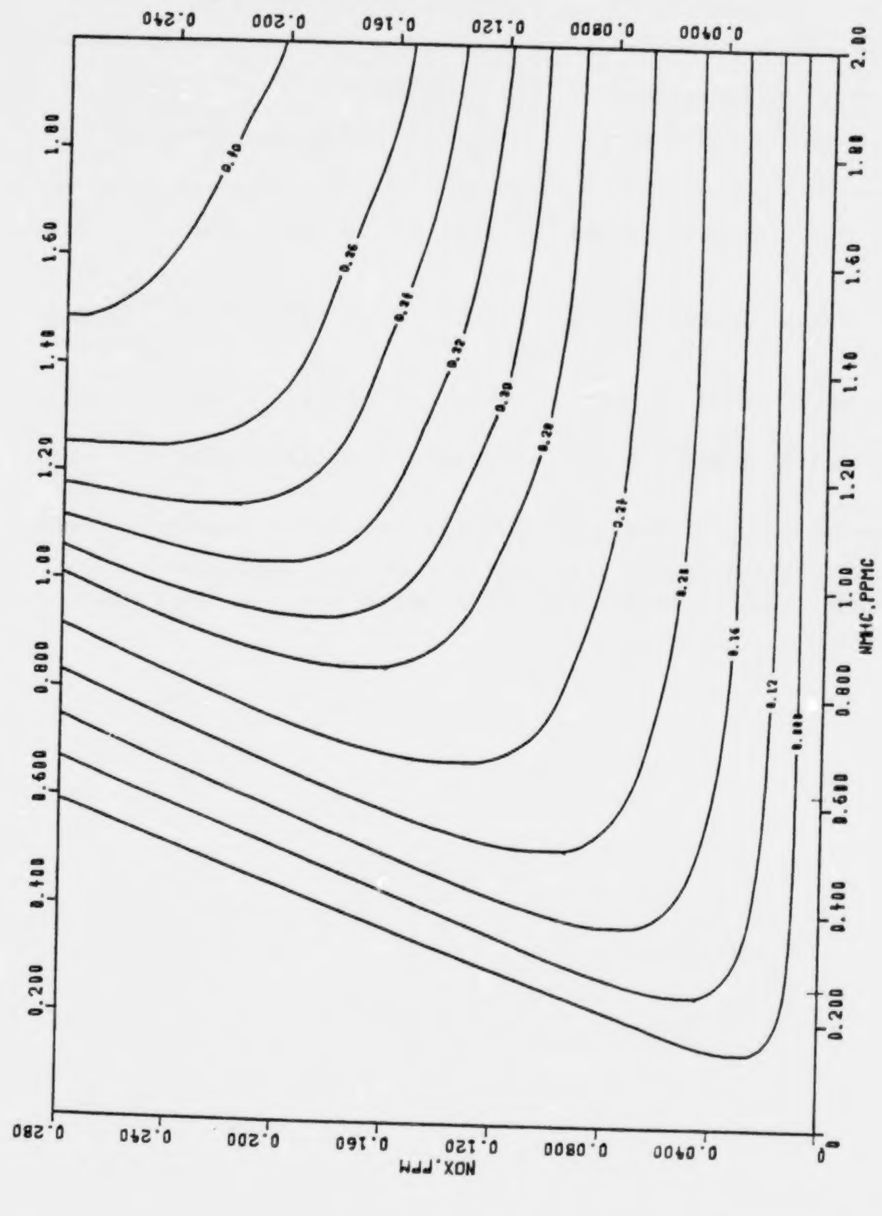


Figure 3-2. Standard Dodge isopleth surface produced by OZIPP computer program.

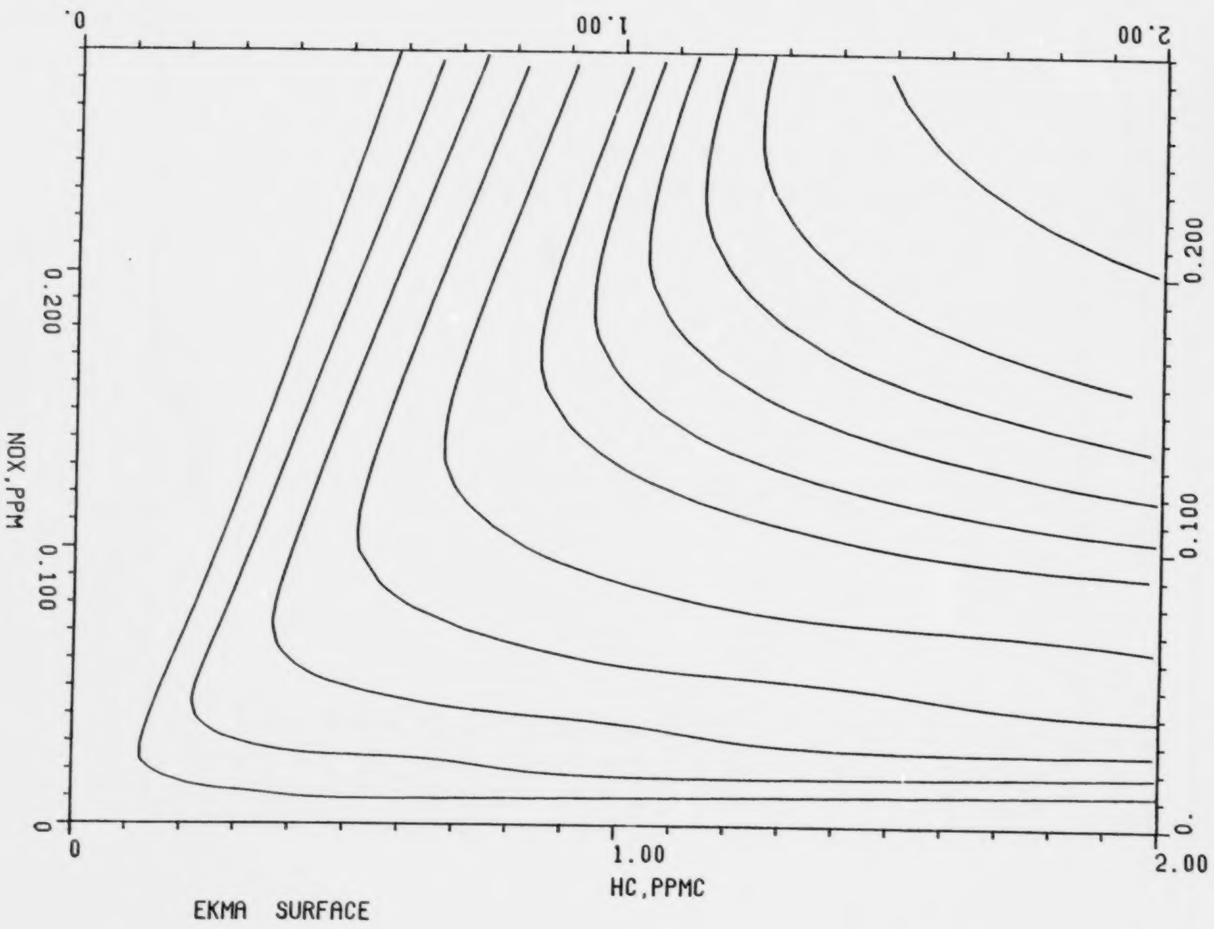


Figure 3-3. Fitted standard Dodge isopleth surface produced by mathematical equation with parameters $c = 0.307$, $n = 0.657$, $\theta = 0.198$, $g = 1.6$, $h = 0.5$, $q = 9.0$, and $r = 1.6$.

TABLE 3-2. REGIONAL MAXIMUM O_3

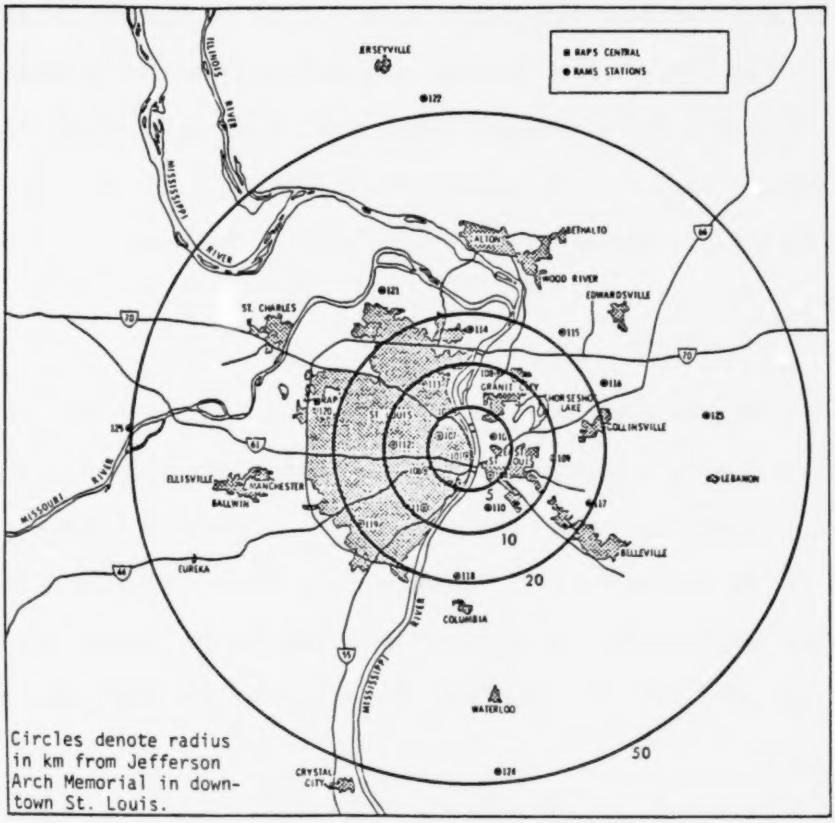
Class	Concentration (ppm)	Observed	Model Expectation
0	0.00-0.01	0	0
1	0.01-0.02	0	0
2	0.02-0.03	1	2
3	0.03-0.04	1	3
4	0.04-0.05	4	3
5	0.05-0.06	15	11
6	0.06-0.07	19	20
7	0.07-0.08	22	22
8	0.08-0.09	29	31
9	0.09-0.10	15	19
10	0.10-0.11	26	26
11	0.11-0.12	26	20
12	0.12-0.13	15	15
13	0.13-0.14	10	15
14	0.14-0.15	14	15
15	0.15-0.16	11	8
16	0.16-0.17	10	6
17	0.17-0.18	6	4
18	0.18-0.19	2	5
19	0.19-0.20	4	4
20	0.20-0.21	3	4
21	0.21-0.22	0	1
22	0.22-0.23	3	0
23	0.23-0.24	2	3
24	0.24-0.25	1	2
25	0.25-0.26	2	1
26	0.26-0.27	0	0
27	0.27-0.28	1	1
28	0.28-0.29	0	1
		242 days	

APPLICATION TO ST. LOUIS

The Regional Air Pollution Study (RAPS) was conceived by EPA early in 1970 to provide a rational scientific basis for the management of air quality. In the program 25 regional air monitoring stations (RAMS) were placed throughout the study region (Figure 3-4). The stations, numbered from 101 to 125, were thought to be located where they would not be unduly influenced by any one source or group of sources. The network was operated for two years, 1975-1976.

The RAPS data base was obtained from EPA. It contained data on 731 days. The 2-year average O_3 concentration was 0.077 ppm. The O_3 standard of 0.12 ppm was exceeded on 105 of the days (14%). The daily maximum O_3 occurred at station 122 on 181 days (25%) and at station 124 on 110 days (15%). These stations were approximately 50 km north and south of the center city. Four stations, 122, 124, 109, and 118, were the sites for the daily maximum O_3 on 62% of the days.

For the purposes of this study, the period June through September of each year was selected. Analysis of HC, NO_x, and O_3 data suggested that this period was a good approximation to a "smog season"; 244 days were included in this period. In choosing the regional O_3 maximum for each day (i.e., a single value per day), only hourly averages between 1200 and 2100 LST were selected. Two days were omitted because no station recorded a maximum above 0.005 ppm; precursors for these 2 days were also excluded.


■ RAPS CENTRAL
● RAMS STATIONS
JERSEYVILLE
122
ILLINOIS RIVER
MISSISSIPPI RIVER
ALTON
BETHALTO
WOOD RIVER
EDWARDSVILLE
66
121
ST. CHARLES
70
114
115
70
113
108
GRANITE CITY
116
HORSESHOE LAKE
RAP
120
ST. LOUIS
125
COLLINSVILLE
124
61
107
112
101
EAST ST. LOUIS
109
LEBANON
106
ELLISVILLE
MANCHESTER
BALLWIN
MISSOURI RIVER
111
110
117
5
119
10
BELLEVILLE
44
EUREKA
118
20
COLUMBIA
55
MISSISSIPPI RIVER
WATERLOO
50
CRYSTAL CITY
126

Circles denote radius in km from Jefferson Arch Memorial in downtown St. Louis.

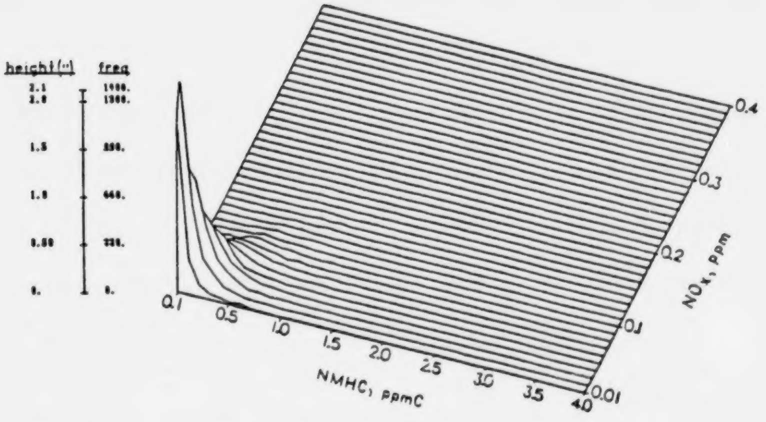
Figure 3-4. The regional air monitoring stations network.

Precursor data were pairs of NMHC and NO_x data for each of the 25 stations for each of the five hourly periods from 7 a.m. to noon LST. There were 18,790 such pairs. The joint distribution is shown in Figure 3-5.

One worrisome feature of the test data set was the presence of negative NMHC values. Because the NMHC concentrations were calculated by subtraction of methane from total HC, it was assumed that the negative values represented very small concentrations. The complete 2-year data set was analyzed to check this.

The negative concentrations were found at the same time as low NO_x values. In 67% of the negative concentration cases, the NO_x value was less than 0.01 ppm. Also, they were present more often later in the morning in the summer months when photochemical reaction is more likely. The month of most frequent occurrence was July (13%) and the month of least frequent occurrence was December (5%). Finally, they were more often obtained from stations away from emissions sources, rather than those in the city region. These results justified the assumption of very small concentrations.

Although setting these NMHC values to zero presented no problem, it did raise the question of what to do about precursor pairs having very low concentrations. Twenty-four percent had NMHC concentrations less than 0.01 ppm. To include all precursor pairs in the analysis in the manner of Post would distort the O_3 surface derived. This is a primary reason for the



JOINT NO_x/NMHC DISTRIBUTION FOR JUNE - SEPTEMBER USING INCREMENTS OF 0.1 ppmC FOR NMHC AND INCREMENTS OF 0.01 ppm FOR NO_x.

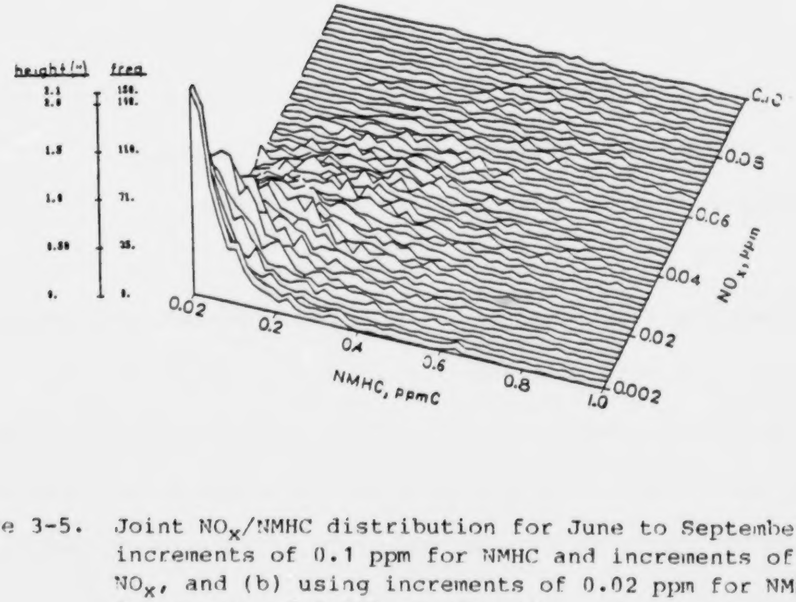


Figure 3-5. Joint NO_x/NMHC distribution for June to September (a) using increments of 0.1 ppm for NMHC and increments of 0.01 ppm for NO_x, and (b) using increments of 0.02 ppm for NMHC and increments of 0.002 ppm for NO_x.

rather different procedure that was followed, that is, the selection of the highest potential O_3-forming precursor pair for each day.

The procedure was applied to determine a St. Louis O_3 surface that would predict the frequency distribution of the regional maximum hourly average O_3 over the June through September periods of 1975 and 1976. The observed O_3 frequency distribution for this period is given in Table 3-1. The Dodge fitted surface was used as the source of the starting values for the parameters (row one, Table 3-2).

The parameters for the best fitting St. Louis O_3 surface are given in the second row of Table 3-2. The surface is shown in Figure 3-6. The precursor pairs selected in the fit are shown in Figure 3-7. The predicted and observed frequency distributions and the cumulative distributions are shown in Figures 3-8 and 3-9.

On only 10 of the 242 days did the chosen precursor pair give a negative value of D (i.e., to the left of the ridge line). Thus the shape of the surface there was not well determined by the data. The major change made to the standard OZIPP/EKMA surface was to move the isopleths farther apart, that is, to lower the parameter c. This fitted surface is quite similar to that obtained empirically by Post for Sydney. This O_3 surface is able to reproduce the bimodal shape of the O_3 frequency distribution (Figure 3-8) and to match the cumulative frequency distribution (Figure 3-9).

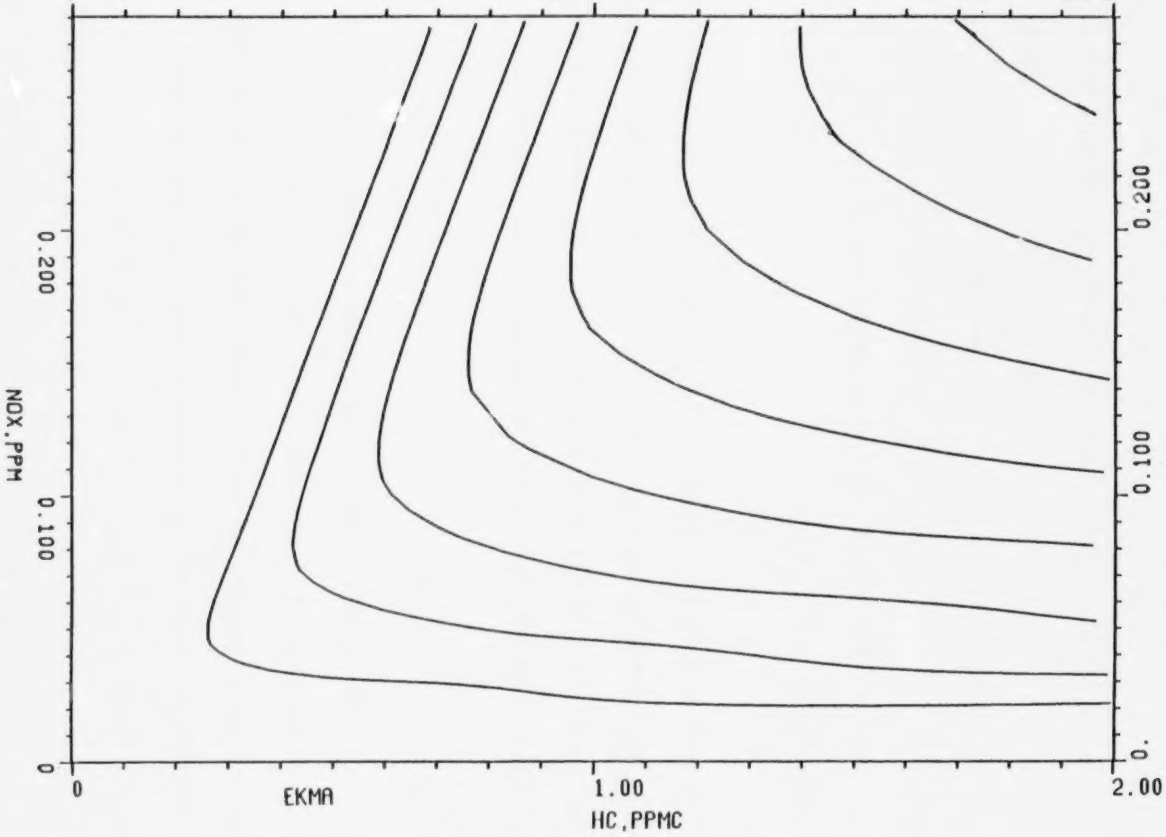


Figure 3-6. Fitted Dodge isopleth surface for St. Louis produced by mathematical equation with parameters: $c = 0.143$, $n = 0.668$, $\theta = 0.192$, $g = 1.54$, $h = 0.529$, $q = 8.78$, and $r = 1.6$.

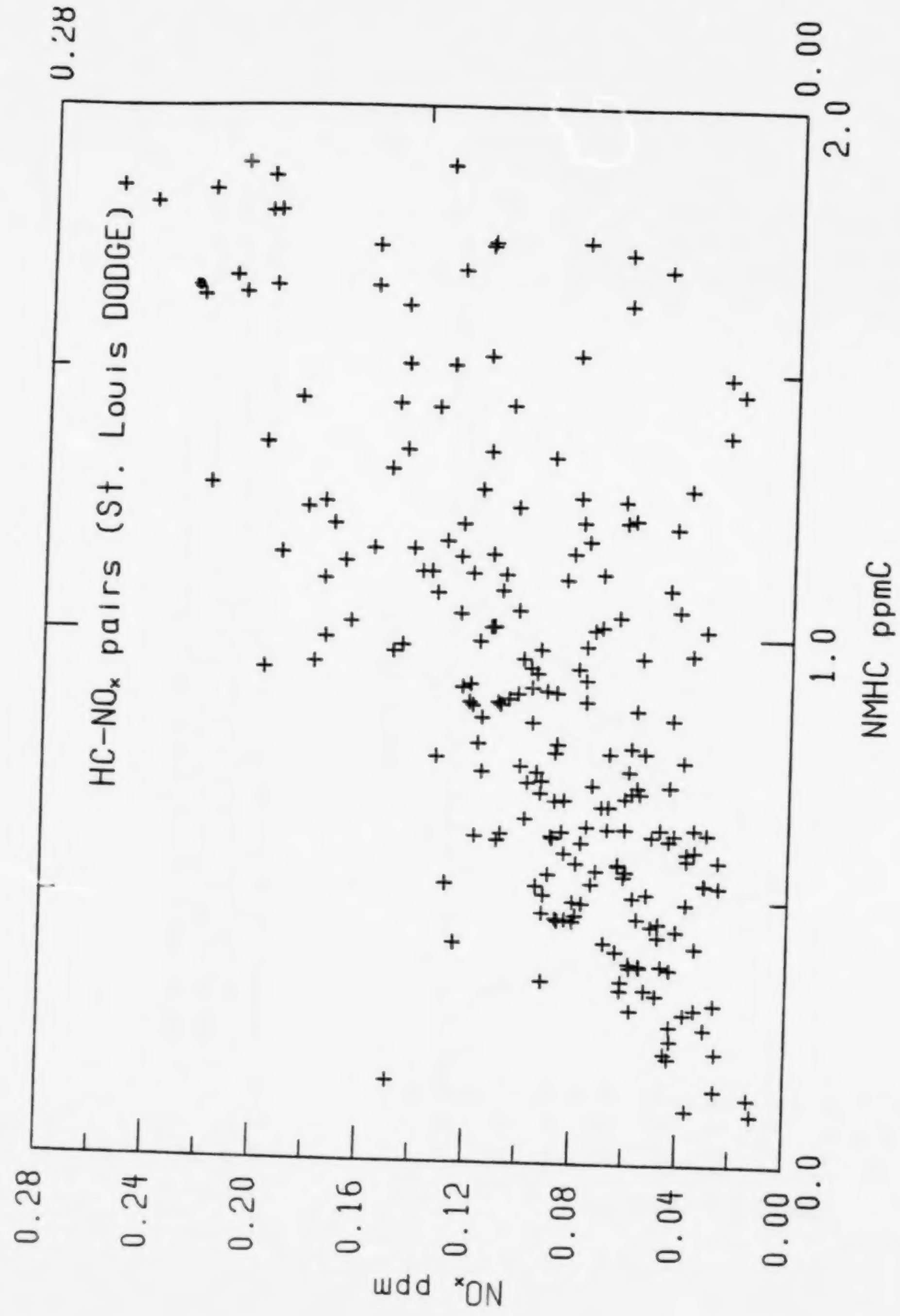


Figure 3-7. HC and NO$_x$ precursor pairs selected by the procedure as having maximum O_3 formation potential using the Dodge isopleth surface (242 pairs, one per day).

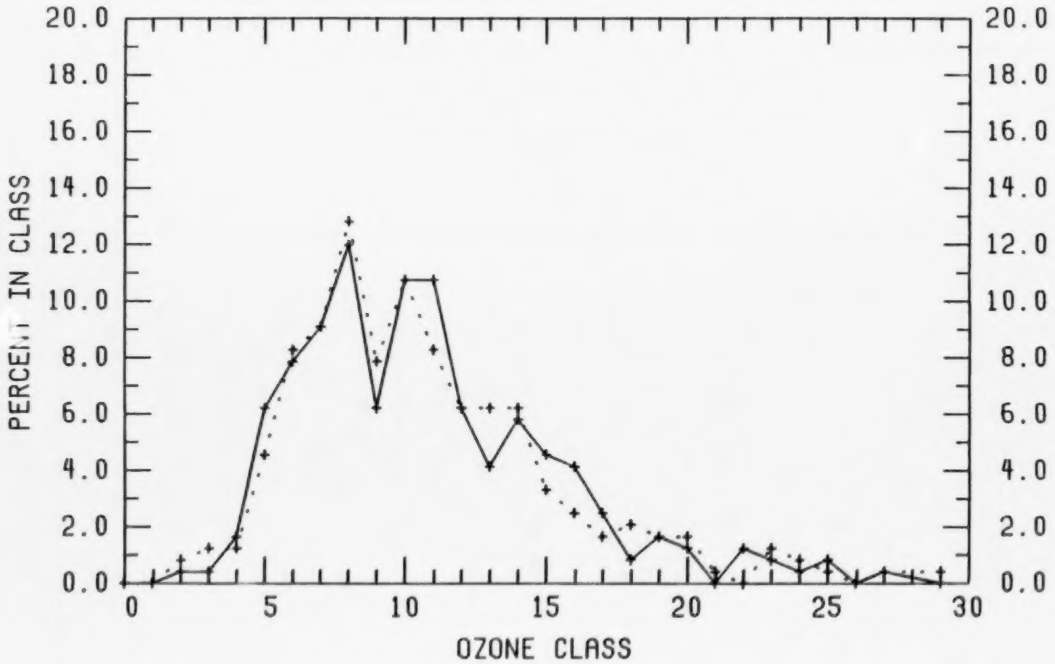


Figure 3-8. Ambient O_3 distribution (solid line) and predicted distribution (broken line) using fitted Dodge isopleth surface and observed HC and NO_x precursor joint distribution (percentage of 242 O_3 days, units for O_3 class 0.01 ppm each class).

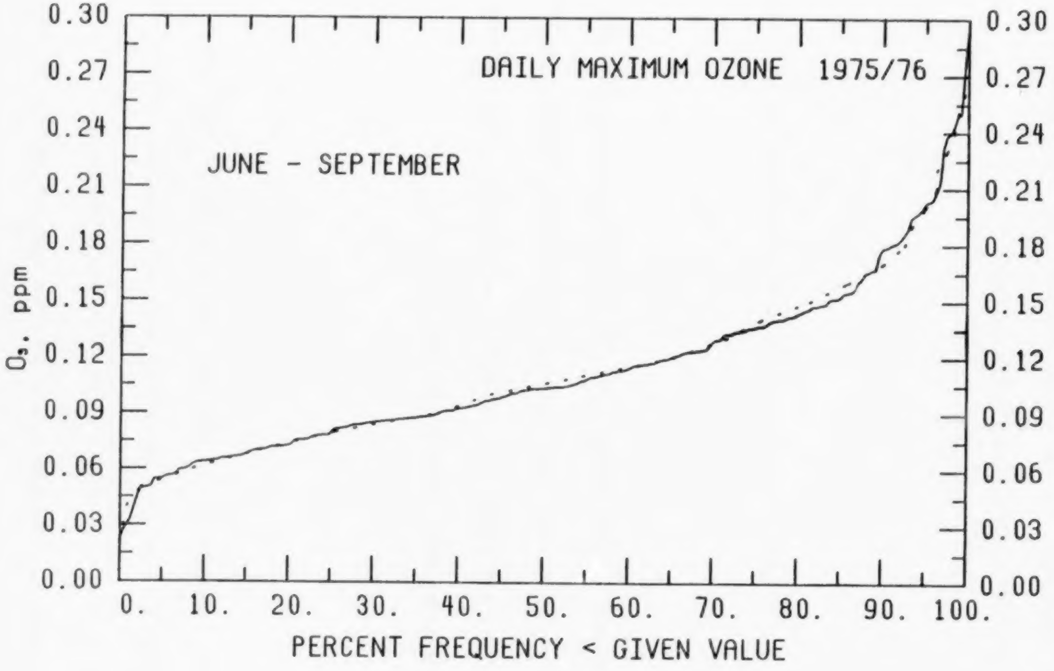


Figure 3-9. Cumulative ambient O_3 distribution (broken line) and cumulative predicted distribution (solid line) using fitted Dodge isopleth surface and observed joint precursor distribution (242 days included).

A chi-square goodness-of-fit test was applied to see whether the differences between the observed and predicted frequencies were significant. The classes were grouped so that only one group had an expected frequency less than five, resulting in 17 groups. Since seven parameters were used in the model, the number of degrees of freedom was nine. Now

$$X^2 = 13.0 < X^2_{(9,\ 0.90)}$$

and the null hypothesis, that the observed frequencies conform to the expected model frequencies, was not rejected.

Because the 242 precursor pairs chosen by the final surface fit were retained, it was possible to analyze their characteristics. More than 87% of these pairs came from the period from 7 to 9 a.m. (Table 3-3) and nearly 85% were provided by the seven innermost stations (Table 3-4).

PARAMETER SENSITIVITY

To test how well each parameter was defined by the data, each was varied by 20%, with the others fixed, and the value of sum of squares noted. The data in Table 3-5 show that the parameter c is the best defined of all the parameters, followed by θ and n. Parameter c is the amount of O_3 produced by 1 ppm of reacting material and is strongly influenced by local dilution. Holton's (1981) study suggests that most chemical mechanisms have a similar value of n, approximately 0.65. This parameter is related to the competition

TABLE 3-3. PRECURSOR PAIRS SELECTED FROM MORNING TIME PERIODS*

Time Period	No Control	80% HC Reduction
0700-0800	62.0	29.0
0800-0900	25.2	29.3
0950-1000	7.0	20.2
1000-1100	2.5	11.2
1100-1200	3.3	9.5

*Percent of 242.

TABLE 3-4. PRECURSOR PAIRS SELECTED FROM 25 STATIONS*

Station	No Control	80% HC Reduction
101	8.7	15.3
102	11.2	3.3
103	4.5	1.2
104	13.2	21.1
105	18.2	15.3
106	9.9	7.4
107	19.0	10.3
Others	15.3	26.1

*Percent of 242.

TABLE 3-5. EFFECT OF PARAMETER VARIATION ON SUMS OF SQUARES* OF DIFFERENCE BETWEEN OBSERVATIONS AND PREDICTIONS

Relative Change	c	n	θ	g	h	q	r
+ 0.20	154.3	53.6	91.5	49.1	41.3	27.0	28.0
-020	187.2	128.4	97.3	48.5	55.3	28.0	26.6

*Best fit surface had a sum of squares of 27.0.

for the hydroxyl (OH) radical among the aldehydes produced and their parent HC compounds. Holton also showed that θ is related to HC reactivity and light intensity; increasing either increases θ. The lack of sensitivity of the parameters q and r is due to only 10 of the precursor pairs giving negative D in Equation (3-2). The reduction of r by 20% actually improved the model fit, but the improvement of less than 2% in the sum of squares for a change of 20% in the parameter was not accepted because of the constraint that the surface shape should be determined by the likely behavior of a chemical mechanism such as the standard Dodge surface.

CONTROL STRATEGIES

Air pollution models have been developed primarily to evaluate alternative control strategies. One of the advantages of the approach pursued in this study is the ease with which different strategies can be tested. It was assumed that a reduction in emissions levels would reflect in the same reduction in morning precursor concentrations. Thus a given reduction was applied to all 18,790 precursor pairs in the original data set and, from the fitted maximum O_3 surface, the future frequency distribution of O_3 for the summer period was estimated for each of the reductions. The predicted distributions are given in Table 3-6 and are compared in Figures 3-10 and 3-11.

TABLE 3-6. CONTROL PREDICTIONS (STANDARD EKMA)
CUMULATIVE PERCENTAGE OF REGIONAL DAILY MAXIMA

MNHC	1.0	0.80	0.60	0.40	0.20	1.00	0.60	0.40
NO_x	1.00	1.00	1.00	1.00	1.00	0.80	0.80	0.80
Ozone (ppm)								
.01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.02	0.0	0.4	0.4	1.2	5.8	0.0	0.4	1.2
.03	0.8	1.2	2.1	2.5	17.8	1.7	1.7	2.9
.04	2.1	2.5	2.9	6.2	43.0	2.1	4.1	7.0
.05	3.3	4.1	7.4	17.8	69.8	5.0	11.2	20.2
.06	7.9	10.7	18.2	33.5	85.5	10.7	22.3	36.4
.07	16.1	21.5	30.6	50.0	91.3	22.3	36.4	50.8
.08	25.2	31.8	43.0	64.5	95.0	34.7	47.1	65.7
.09	38.0	43.8	52.9	75.2	97.9	44.6	59.9	76.4
.10	45.9	53.7	65.3	83.1	99.2	57.0	69.8	83.9
.11	56.6	63.2	73.1	90.1	100.0	64.9	78.1	90.1
.12	64.9	70.2	81.0	94.2		71.9	85.1	94.6
.13	74.1	77.7	86.4	96.7		78.1	89.7	95.5
.14	77.3	83.9	89.3	97.9		85.5	90.5	97.5
.15	83.5	87.2	91.3	98.3		87.6	93.8	97.5
.16	86.8	89.7	95.0	98.8		89.7	95.5	98.3
.17	89.3	92.1	95.9	99.2		92.6	97.5	99.6
.18	90.9	93.8	97.5	100.0		94.2	97.5	99.6
.19	93.0	95.5	97.5			95.5	97.5	100.0
.20	94.6	96.7	97.5			96.7	99.2	
.21	96.3	97.5	99.2			96.7	99.2	
.22	96.7	97.5	99.2			97.9	99.6	
.23	96.7	98.8	99.2			98.8	99.6	
.24	97.9	99.2	99.6			99.2	100.0	
.25	98.8	99.2	99.6			99.2		
.26	99.2	99.6	100.0			99.6		
.27	99.2	99.6				100.0		
.28	99.6	99.6						
.29	99.6	100.0						
.30	100.0							

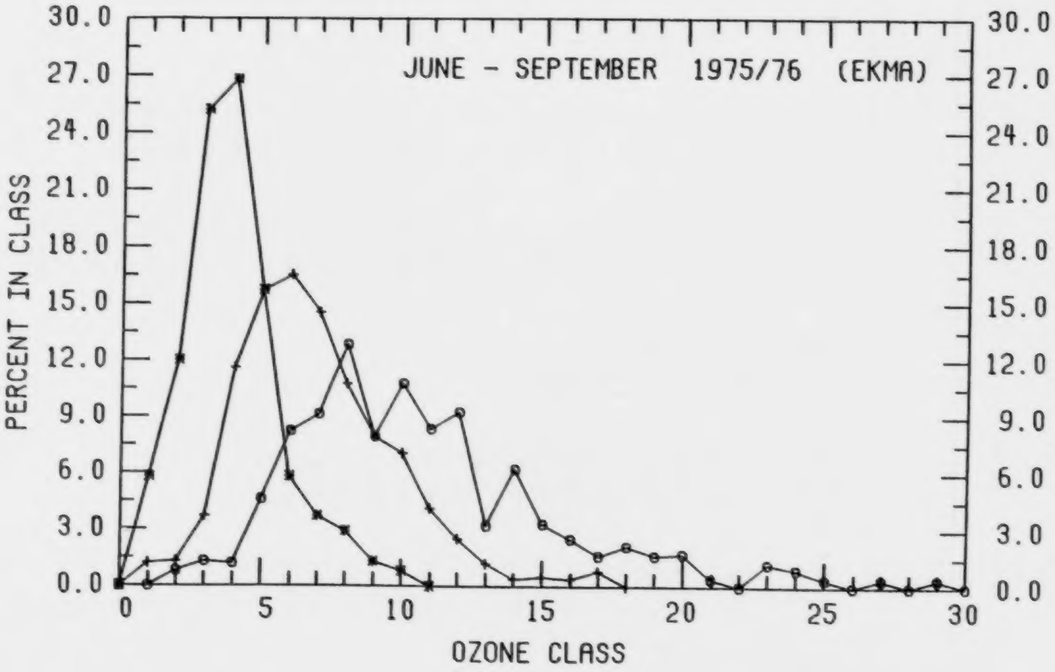


Figure 3-10. Predicted O_3 distributions using fitted Dodge isopleth surface and joint precursor distributions in which the HC concentrations have been reduced by indicated percentages; NO_x were not reduced (percentage of 242 days, 0.01 ppm each O_3 class).

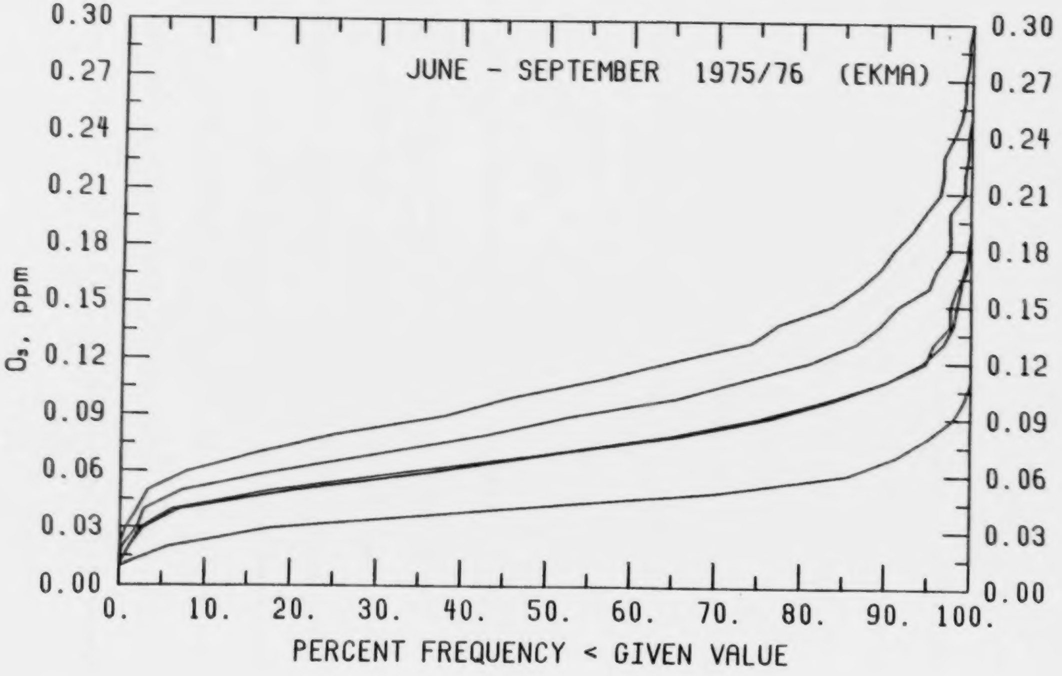


Figure 3-11. Cumulative O_3 distributions as in Figure 3-10. In addition to 60% reduction of HC only, a simultaneous 20% reduction in NO_x is also shown.

In the calculations the whole precursor-pair data set was used. It was not assumed that the precursor pairs that generated regional maximum O_3 under a control strategy calculation were the same as those under either no control or an alternative control.

Given two points representing precursor pairs of similar concentrations, the procedure for selection will choose the point that is closer to the ridge line. Under different control options all of the precursor points are moved relative to the ridge line, and hence the set of selected points will change slightly (see Tables 3-3 and 3-4). This facility in the procedure tends to make it more conservative than other simple modeling exercises (EKMA, for example).

The model suggested that for the St. Louis region NMHC control, rather than NO_x control, was the appropriate path to follow without considering the question of relative costs. This is also in agreement with the findings of Post (1979) for Sydney. The model also indicated that under 60% NMHC control a standard of 0.12 ppm would be exceeded on about 6% of the days in the 4-month period (i.e., 7 days); under 80% control a standard of 0.12 ppm would be met virtually all the time. The joint HC-NO_x distribution for 80% reduction is shown in Figure 3-12 for comparison with that for no control in Figure 3-7.

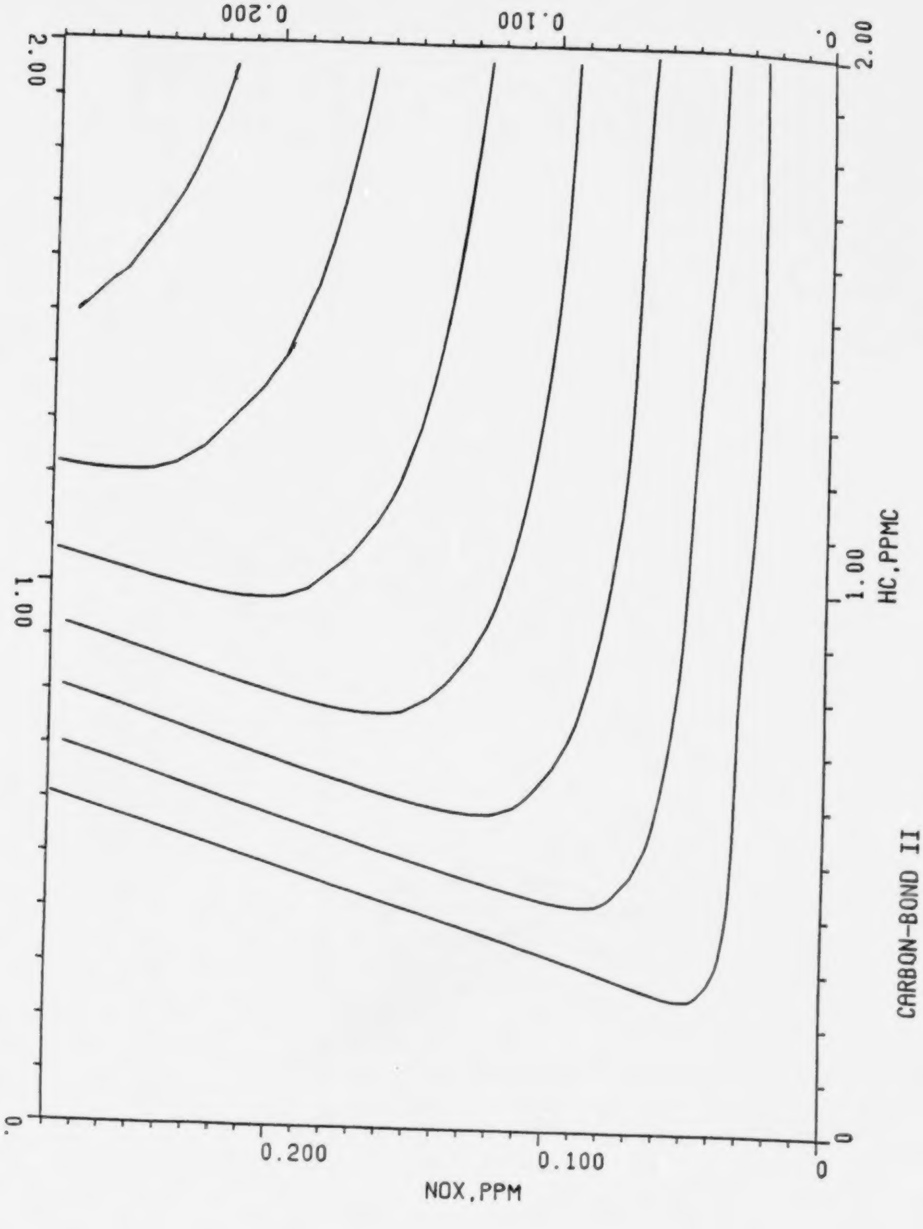


Figure 3-12. HC and NO_x precursor pairs selected by the procedure as having maximum O_3 formation potential for 80% NMHC reduction using the Dodge isopleth surface (242 pairs).

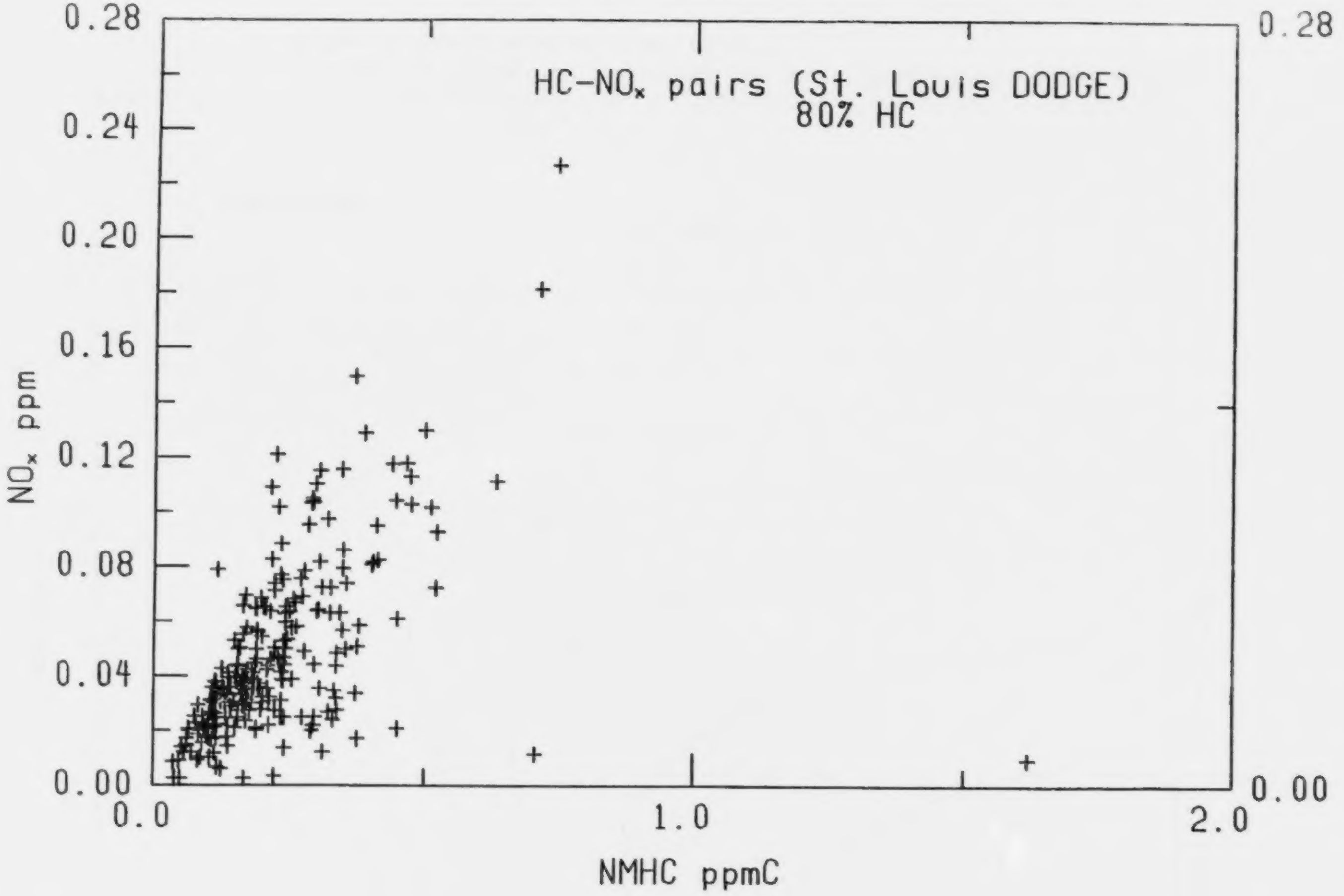


Figure 3-13. Fitted Carbon Bond II isopleth surface for St. Louis produced by mathematical equation with parameters: $c = 0.140$, $n = 0.639$, $\theta = 0.209$, $g = 1.70$, $h = 0.562$, $q = 5.4$, and $r = 1.5$.

MECHANISM SENSITIVITY

It has already been noted that in this application the maximum O_3 surface was specified poorly to the left of the ridge lines. This section of surfaces, generated by simulations with chemical mechanisms under fixed meteorological conditions, is also the least well defined, that is, it is the section most sensitive to changes in chemical mechanisms (Jeffries et al., 1981). For this reason, part of the study was repeated using a different initial surface.

Holton (1981) supplied parameter values which give a maximum O_3 surface generated using the Carbon Bond II mechanism used currently in the Systems Application, Inc. urban airshed grid model. The surface resulted from simulations under summer-solstice light and medium HC reactivity. The parameter values are given in row three of Table 3-7.

Using the same data base, the iterative procedure described previously was followed to determine a surface with the same general shape as this initial surface but which produced a similar O_3 frequency distribution to that observed. The surface is shown in Figure 3-13 and the parameters are given in row four of Table 3-2. Note that the ridge line parameters are quite similar to those obtained with the Dodge surface as starting conditions, but the left-side parameters are quite different. The O_3 frequency distribution was not quite as good a fit (Figures 3-14 and 3-15) as that achieved using the standard Dodge surface as an initial surface. The initial Carbon Bond II

TABLE 3-7. CUMULATIVE PERCENTAGE OF REGIONAL DAILY MAXIMA CONTROL PREDICTIONS (CARBON BOND II MECHANISM)

MNHC	1.0	0.60	0.40	0.20	0.40
NO_x	1.0	1.00	1.00	1.00	0.80
Ozone (ppm)					
.01	0.0	0.0	0.0	0.0	0.0
.02	0.0	0.4	0.8	2.1	0.8
.03	0.8	2.1	2.1	13.2	2.9
.04	2.1	2.9	5.0	37.2	7.0
.05	2.9	8.7	16.5	66.6	20.7
.06	9.5	17.8	33.5	83.5	34.7
.07	18.2	30.2	48.3	90.1	49.2
.08	26.4	43.8	63.2	95.0	66.9
.09	39.7	55.0	74.4	98.0	77.3
.10	49.2	66.1	83.5	98.8	88.5
.11	60.7	75.2	90.5	99.6	90.9
.12	69.4	82.2	95.0	100.0	94.6
.13	75.6	88.8	96.7		95.9
.14	81.8	89.7	97.9		97.5
.15	86.8	93.0	98.3		97.5
.16	89.3	95.0	98.8		98.8
.17	90.9	97.1	99.6		99.6
.18	93.0	97.5	100.0		100.0
.19	94.6	97.5			
.20	96.3	99.2			
.21	96.7	99.2			
.22	97.1	99.6			
.23	98.3	99.6			
.24	99.2	100.0			
.25	99.2				
.26	99.6				
.27	99.6				
.28	100.0				

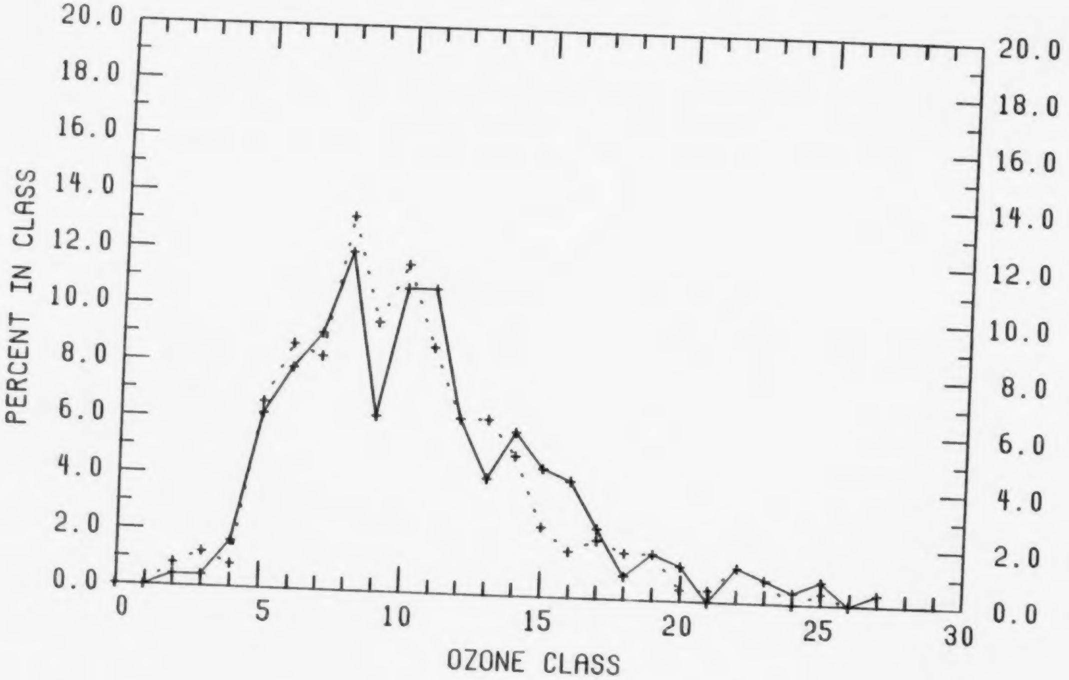


Figure 3-14. Ambient O_3 distribution (solid line) and predicted distribution (broken line) using fitted carbon-bond isopleth surface and observed HC and NO_x precursor joint distribution (percentage of 242 days, 0.01 ppm for each O_3 class).

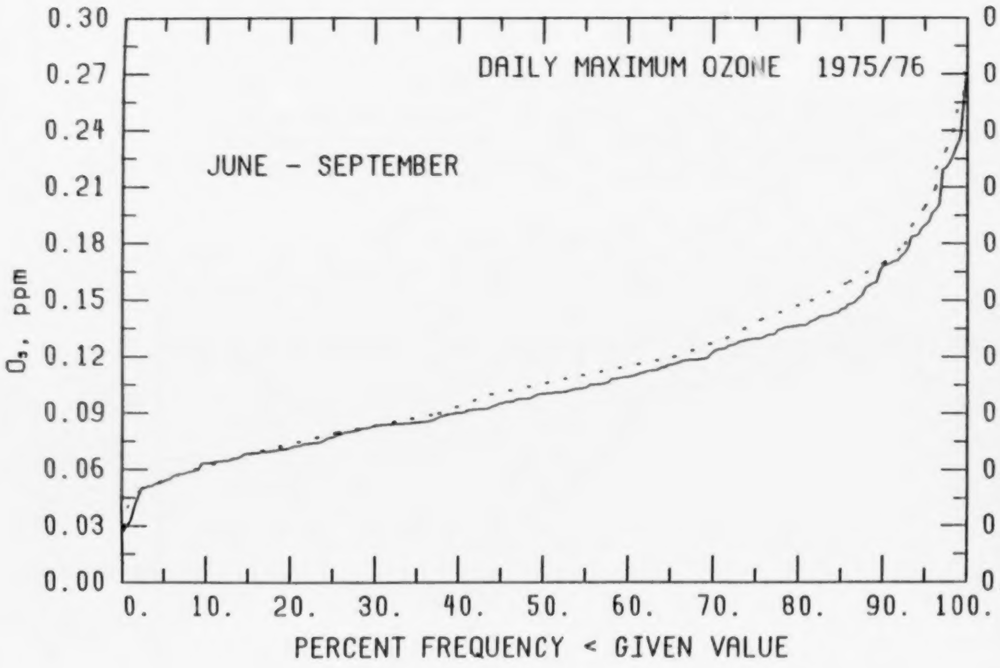


Figure 3-15. Cumulative ambient O_3 distribution (broken line) and cumulative predicted distribution (solid line) using fitted carbon-bond isopleth surface and observed joint precursor distribution (242 days included).

surface, however, was substantially different from the Dodge surface. A carbon-bond surface of lower reactivity or lower light intensity might have generated a better fit.

Some of the control strategies tested with the previous surface were retested (Table 3-7). The maximum O_3 distributions predicted by the two surfaces for controlled conditions are very similar (Figures 3-16 and 3-17). This is somewhat surprising since, as HC concentrations are reduced, more precursor points move across the ridge to the region of negative D, the region where the two surfaces are most different. The reason is that different precursor pairs are responsible for the maximum O_3 under the control strategy than under standard conditions. Once precursor points move across the ridge line into the region of negative D, other points with less NO_x will be likely to produce more O_3 and will be selected to replace them. Thus there is a decrease in the NO_x concentrations of the precursor points chosen as the HC control is increased (Table 3-8). The tendency of the procedure is to choose points closer to the ridge line, because this is where maximum O_3 production occurs, and near the origin at the ridge line the two surfaces are nearly identical.

DISCUSSION

There are three assumptions in this technique for evaluating emissions control strategies in relation to the production of O_3 in urban atmospheres. The first is that there exists a simple surface which embodies the probability

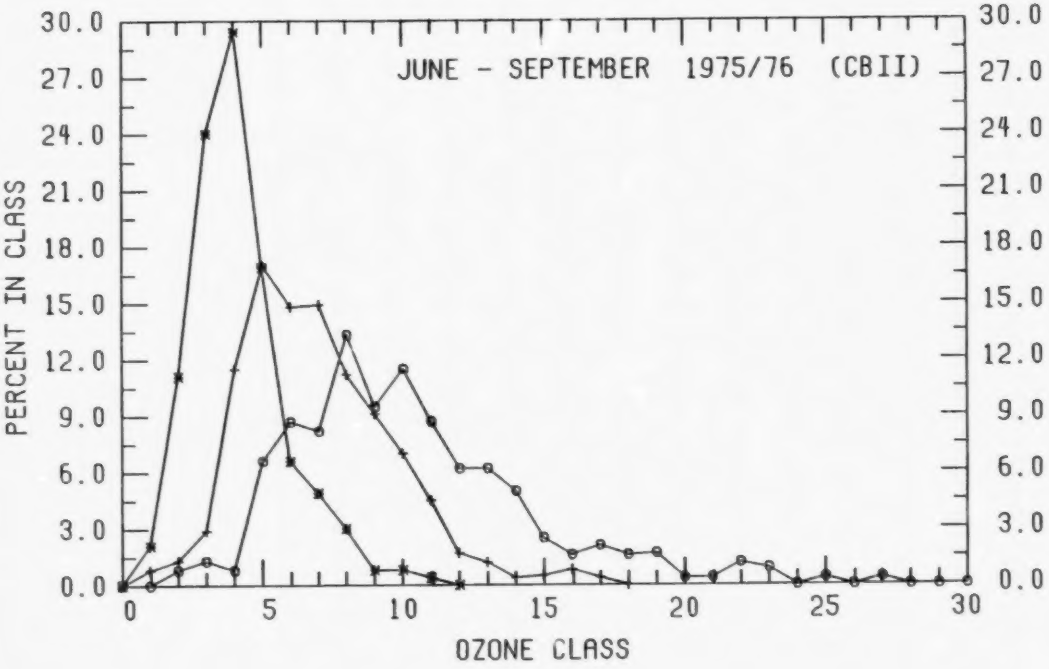


Figure 3-16. Predicted O_3 distributions using fitted carbon-bond surface and joint precursor distributions in which the HC concentrations have been reduced by indicated percentages; NO_2 was not reduced (percentage of 242 days, 0.01 ppm each O_3 class).

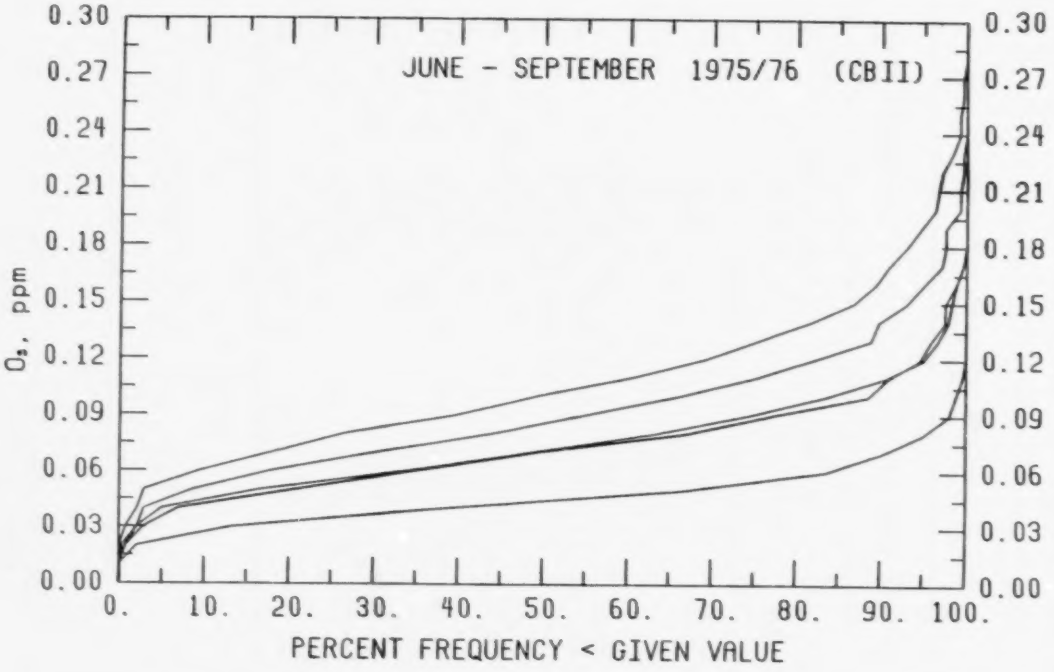


Figure 3-17. Cumulative O_3 distributions as above. In addition to 60% reduction of HC only, a simultaneous 20% reduction in NO_x is also shown.

TABLE 3-8. MAXIMUM O_3 PRECURSOR PAIRS

	Cumulative Percentage			
	Carbon Bond II		Standard EKMA	
NO_x (ppm)	1.00 NMHC 1.00 NO_x	.20 NMHC 1.00 NO_x	1.00 NMHC 1.00 NO_x	.20 NMHC 1.00 NO_x
.01	0.0	2.9	0.0	4.5
.02	1.7	11.6	1.7	14.1
.03	4.1	31.0	4.5	33.9
.04	9.9	53.7	11.6	56.6
.05	18.2	63.2	19.4	67.4
.06	26.0	70.2	27.7	74.0
.07	35.1	78.1	36.0	81.8
.08	43.0	83.1	43.8	86.4
.09	50.4	86.8	52.1	89.7
.10	57.4	89.3	59.1	91.3
.11	64.5	93.4	64.9	94.6
.12	71.1	96.7	71.1	97.5
.13	75.6	97.9	75.6	98.8
.14	78.5	97.9	78.5	98.8
.15	81.4	98.3	81.4	99.2

distribution of summertime conditions in a given region and which produces a distribution of maximum O_3 as a function of morning NMHC and NO_x concentrations. This implies that it will be valid to use the surface to determine O_3 distributions for a variety of precursor distributions. The second is that it is possible to determine the general shape of the surface from simulations using photochemical mechanisms derived from smog chamber studies. The third is that parameters can be found which produce an acceptable fit to air quality data from the region and which maintain the surface shape.

In this revised application of the Post method the procedure operated in a stable and consistent manner. Once the surface was determined it was a simple matter to determine the effects of a number of control strategies.

The reasonableness of the assumptions used can be established by applying the procedure to different regions, by checking the conclusions against more complex photochemical models, and by applying the procedure to different summertime periods in the same region where there have been changes in precursor concentration levels. The technique has given a good description in two large cities: Sydney, Australia, and St. Louis, MO.

CONCLUSIONS

Maximum O_3 surfaces can be constructed from air quality data and kinetic-mechanism-derived surfaces to evaluate emissions control strategies.

Nonmethane hydrocarbon emissions control is the most effective strategy to follow for the St. Louis region. Using 1975 and 1976 as a baseline, a reduction of 70 to 80% NMHC is predicted to achieve the 0.12-ppm O_3 standard.

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WORKSHOP COMMENTARY

ESCHENROEDER: How sensitive is the O_3 frequency distribution to the number of sample days that you choose?

JEFFRIES: I don't know. We didn't have the opportunity to go back through and try dropping out half the days and a third of the days. Keith Post dropped out half the days and got the same answers.

ESCHENROEDER: He had how many, 800?

JEFFRIES: He had 2 years of summertime data, 6 months. He halved the distribution; in other words, half the HC and NO_x, and half the O_3. He calculated the frequency distribution for each half and got the same answers as before. The distributions for the whole year are, of course, different from the distributions for just the smog season.

ESCHENROEDER: I was thinking that given a certain interval a sparser sample would give the same results.

JEFFRIES: We don't know how stable the process would be. It's a question of how good the statistics might be as the numbers drop below a couple of hundred points. Post had 800 half-hour precursor pairs, and we started out with 18,000 hourly pairs and reduced that to 242. The problem is, how many pairs out of 242 could be misplaced before significant errors ensue.

As it turns out, the major difference between a Dodge and a carbon-bond surface is in one little region down in the corner. Of course, Carbon Bond II picks a different set of points than does Dodge. Each mechanism is going to choose its own set of points out of the 18,790 initial pairs; assuming that they are reasonably close, the method would have chosen points very similar both for Carbon Bond II and for Dodge. Overlaying the carbon-bond isopleth on top of the Dodge points, we note the Dodge isopleth contains a few points counted above, whereas in the carbon-bond isopleth they're counted in the interval below. It's very subtle. That little difference of curvature can change the fit to the frequency distribution.

The method does converge. We tricked the convergence method, because we make it converge on the difference between the intervals, which is a little unusual in terms of the way the algorithm was derived. The algorithm is intended to converge the absolute O_3 versus the predicted O_3, and we're converging the frequency. So it's a strange operation, and it's not as sensitive as we like. However, once the values get this close, one can almost do a better job of fitting by inspection.

ESCHENROEDER: But the appealing thing is that the frequency is really what you want in the end to formulate the control strategy.

JEFFRIES: Yes. I spent a long time trying to argue with Keith Post over whether this method worked, or whether it was just coincidence. Keith would always respond that it must be in the model because the model reproduces the observed frequency distribution. So if O_3 aloft is important, fine, it's already in the isopleth diagram because the precursors reproduce the frequency distribution. In fact, it's hard to argue with a model that fits well.

McRAE: Did you look at the distribution of O_3 to see how it compares with a conventional log normal distribution?

JEFFRIES: Yes. It's very log normal except for wintertime. It's log normal for the whole period, but it's not log normal for this subset that we're looking at here.

ESCHENROEDER: Didn't you have one log-versus-probability plot for frequency distribution that showed curvature?

MARTINEZ: That was linear probability.

JEFFRIES: No. I do have a strictly log probability plot fitted with the points from a log normal model and you can't tell the difference. Chi-square tests indicate they are the same.

McRAE: The second question I have is a little bit more general. Since you're introducing the whole notion of probability to control strategy design, what would your recommendations to agencies be about how they would use this information to design control strategies to meet standards which don't match this same idea? That is, what does this procedure give you that's different from the conventional approach to the problem from the control agency point of view?

JEFFRIES: The current guideline that's out recommends looking at 5 HC-to-NO_x ratios for 5 days at each of the sites that you're concerned with, which is some kind of subset of the whole precursor distribution. Here we are concerned with the entire precursor distribution. This method allows for the fact that, unlike the conventional EKMA approach where you work with the one point and take it over to the limited side, here it's similar to the airshed model results, in that the airshed model in the future would predict some O_3 where it's not predicted today, because that's the optimal point for production of O_3 under the control conditions. With the standard-EKMA approach, you don't know that point because you're not dealing with all of the data. The complicating feature is that all the data are required, including the ambient measurements. This raises the issue of how many data are really necessary. I don't know the answer to that yet.

MEYER: Do you have any feel, based on the work you have already done, of how applicable this method might be in other cases, say, if the O_3 transported into the area were to change in the future, or if some diurnal emission pattern were to differ radically?

JEFFRIES: If transported O_3 has a significant impact on the generated isopleth surface, and that somehow goes away in the future, the isopleth would no longer fit the case. The question would have to be, how sensitive is the O_3 frequency distribution to the transported O_3; I don't know how to answer that. It may be possible to relate this isopleth back to chemical and meteorological conditions that produce it. I can't say, for example, that if I make a simple trajectory model run and produce an isopleth from a given mechanism, with a given amount of dilution and all the other input, the isopleth is absolutely correct. All I can say is that the isopleth would be within the bounds that would be produced from such a run. Taking the chemical model, you can run the model for the impact of O_3 aloft and determine the effect on the isopleth. The problem is that you can't go beyond the initial data base. Whatever is important in controlling O_3 now is captured in the model, and the assumption is that that's stable across the design period.

MEYER: Do you think there is some way of factoring out the nonmeteorological inputs?

JEFFRIES: No. One cannot say that the O_3 measured at a site is caused by so much O_3 aloft, so much emissions from here, and so much emissions from over there.

MEYER: Rather than having HC-NO_x pairs, how about using a triplet: HC-NO_x plus transported O_3?

JEFFRIES: I hadn't thought about that process.

WHITTEN: I'm troubled with this method because I have a hard time feeling that it is really related to control of emissions in any way, and that it's going to respond that way under future controls. I feel that the test that you have here, namely, the shape of the frequency distribution, may not be a severe enough test. My experience is that no matter what chemical or meteorological inputs are used, the same general "L"-shaped isopleth always results. If you then skew them around to fit your data base, as with your factor, the result would be a similarly shaped curve and a similar shape distribution, and hence a similar O_3 distribution.

JEFFRIES: It is not true that you can change the parameters and get a good fit.

WHITTEN: What I mean is parameters in the chemistry and parameters in the meteorology.

JEFFRIES: I know pretty much the relationships between the parameters that fit the surface and the parameters of chemistry. But I know if I change the rate constant in the chemistry it's going to change the parameter of the surface.

WHITTEN: And that will alter the result.

JEFFRIES: No. The dominating factor here is meteorology, not chemistry.

WHITTEN: Yes, and my experience is that if you alter the meteorology you still get a similarly shaped curve.

JEFFRIES: The point here is that there is a number or a set of numbers that characterize the conditions in St. Louis during this period sufficiently well that when you put the observed HC-NO_x pairs on them, you get the observed O_3

distribution out of them. The surface is a model that somehow captures all the factors that are important in going from initial concentrations to O_3.

WHITTEN: My question is, do you feel that if you put in some obviously faulty meteorology, would you produce a frequency distribution that would definitely show up as being wrong?

JEFFRIES: Yes, it will not fit. I start with simply a description and modify it. It's equivalent to taking the Dodge isopleth program, and changing the mixing heights in it repeatedly until I get an isopleth with satisfactory fit.

WHITTEN: Basically your dilution is a kind of factoring.

JEFFRIES: Yes, the results say that the frequency distribution can be fit with the observed precursor distribution by simply taking the Dodge isopleth surface and changing the initial and final mixing heights until a similar isopleth appears. The relative spacing, for example, up the isopleth, is a function that is competition between the aldehydes produced and apparent HC's in the mechanism. That's why the carbon-bond isopleth has a different curvature on it than does Dodge's. Dodge has different rate constants for OH reacting with the aldehydes than in OH reacting with apparent organics.

The key factor is for so much mass shoved in, how much O_3 do you get out? And that's the c factor. And in effect I can control that by simply controlling dilution. Now, there is some fine tuning that can be done. To the extent that your mechanism and her mechanism represent approximately the same chemistry of NO_x and HC's, yes, they will both give generally the same-shaped isopleth, but if you change a particular mechanism, you won't get an isopleth that will give you the same answers. What I have done is produce a nonchemical way to look up the parameters that you'd have to solve for by repeated iterations of the chemical parameters.

I did want to say that the method obviously assumes that there is a linear relationship between emissions and precursor concentrations; and that over a long time period that's probably not a bad approximation.

WHITTEN: But as you know, I showed you yesterday, there is discrepancy --

JEFFRIES: If O_3 aloft is important in the formation of O_3, it will influence the frequency distribution observed; since the model already reproduces that, it's already in the model.

WHITTEN: And if that changes?

JEFFRIES: If that changes, then nothing can be done about it.

WHITTEN: My other questions are, your system goes through and picks up these pairs of HC amounts which on a given isopleth diagram produced the worst O_3

for that particular day; have you ever gone back and looked at your 242 pairs, just a few of them, to see if the wind was blowing in the direction where the maximum O_3 was produced?

JEFFRIES: There is no effort to relate the O_3 produced on that day and the precursor observed on that day. I don't want to because what is the probability that a measured precursor pair is going to actually make it to a station and be measured? I suspect it's quite low.

WHITTEN: I was just wondering if the wind was blowing in the opposite directions on some of those days.

JEFFRIES: I don't know. What the method does assume is, if you measured that pair, there is some other pair that has the same concentration you didn't measure that does make it to a station that you do observe.

WHITTEN: I can agree with that.

JEFFRIES: So it's that kind of statistical relationship. I'm not saying that the pair that I kept is the pair that made the O_3, not at all; that is what Dr. Martinez does. He says that the pair he kept was validated and he puts it on the isopleth diagram. The O_3 he predicts is compared with the day's O_3. I don't do that. I just say that tells me how often I ought to observe that O_3.

MARTINEZ: I did that for the Houston data, and in general the high O_3 observed agrees with the wind direction.

JEFFRIES: It's clear here that 62% of the time the O_3 occurs either due north or due south of the city and most of the time the high concentrations are in the middle of the city.

WHITTEN: You seemed to indicate that many of the maximum pairs that you observed occurred at the hour of 7 a.m..

JEFFRIES: 7 or 8 a.m.. That was under the no-control condition. Under the control condition they spread out. So do the stations.

WHITTEN: Did you look at any earlier hours?

JEFFRIES: No.

WHITTEN: So it looks to me like the earliest hour you looked at was 6 a.m., and that was the most important one. And so I would have a little more interest as to what about 4 a.m. and 5 a.m.; maybe they would even be better, so it's hard to say. It's kind of at the edge of your artifact cut-off.

JEFFRIES: That's right. I'm comfortable with the cut-off at noon, as concentrations drop away dramatically.

WHITTEN: 6 a.m. sounds good until you find out that that happens to be the most important one, and then it's not so good anymore.

TRIJONIS: Statisticians look at an awful lot of frequency distributions of aerometric data. Maybe it's nothing to be concerned about, but I remember you said that there were two dips in the HC data; those are certainly statistically insignificant from the 224 points, but today you said something about the O_3 being bimodal because it had one dip in the sense there were less points between 9 and 10 a.m. than there were between 8 and 9 a.m. and 10 and 11 a.m. What concerned me is that I don't think it is bimodal. I think that's just a statistical error. Would it affect the results? I think that dip is a minus rather than a plus. I don't think it's the type of thing you want necessarily to fit.

JEFFRIES: It was in the observed data.

TRIJONIS: But if it's a statistical fluke in the observed data, would that affect your results?

JEFFRIES: I would not be willing to say that it's a statistical fluke in the observed data. I think it really is true that during that period there were fewer days with that concentration.

TRIJONIS: There were, but if you took 5 more years, I don't think you would see that.

JEFFRIES: That's probably true. And in 5 more years we wouldn't have the same kinds of fluctuations in the HC data, either.

TRIJONIS: Right. But is there any problem with overfitting in the sense that you're fitting a dip in the data that just happens to be there? Are you overfitting statistical flukes rather than the smooth distribution? You weren't fitting the smooth distribution, you were fitting the random fluctuations in the distribution.

JEFFRIES: The point is that the precursor distributions in the isopleth diagram reproduced those random fluctuations, so they're not necessarily random. And they were in the precursors. What it says is that the precursor distribution is everything.

TRIJONIS: They were based on 242 kept points. And you'd have 18 in one, 13 in another, and so on. If you had enough data points, you would have had 17, 16, 17, 14, 13, a nice smooth distribution. What disturbs me is the fact that your method was geared to fit these fluctuations.

JEFFRIES: The method is geared to minimize the sum of the squares; the difference is between the two distributions. Period. That's all it does.

TRIJONIS: Right. But in that sense it's fitting statistical irregularities; overfitting, in a sense.

JEFFRIES: You cannot say they're statistical irregularities. They are actually in the observed data.

TRIJONIS: Yes, they're there, but in the observed data it's not a smooth distribution and you're fitting the outlying points.

Also, I thought there was something to what Dr. Whitten was saying in that if you took a nonsense isopleth, could you also get it to give good results? I was wondering if it had something to do with the fitting problem.

JEFFRIES: I've got observed O_3 data and I've got observed HC data and I've got a model and I put the observed HC-NO_x data in and I get the observed O_3 data out; that's all I can say. The isopleth is an isopleth that can be related to standard chemical mechanisms and operated under very reasonable conditions in the functions. There is nothing unusual or odd or weird about the isopleths.

TRIJONIS: Maybe there's a different answer. You know what data mining is -- when you have a small set of data and you're trying to represent in some sense a continuous distribution; only you have 242 points. Data mining is when you overfit your parameters to the particular set of data you have. You don't think there is any possibility of that type of problem?

GIPSON: The question here is, what is the likelihood of getting a spurious fit to your frequency distribution, and how would you recognize the spurious fit, if you got it?

JEFFRIES: Well, we give the typical chi-square test of the two frequency distributions to see the fit. I suspect if you're allowed to adjust the isopleth surface enough, you could probably find other surfaces that would also fit. That's why we decided to start with a surface that looked like a surface produced by chemical mechanisms, under reasonable conditions, so that the surface that we get is not obviously weird. It's not a weird isopleth. Clearly, there are two slightly different isopleths that came out of Carbon Bond II and out of Dodge. One of them gives a superior fit compared to the other and you can inspect the data against the lines and see why it gives a superior fit, and we could easily change a slight parameter in the Carbon Bond II fit and make it come out just as good.

GIPSON: The question really is, when any model fails, can you recognize it as failing? What will you have to do to a chemical model, statistical model, or whichever, so that it would not reproduce the frequency distribution?

JEFFRIES: Very simple. It doesn't fit the frequency distribution. It would overpredict.

GIPSON: And how would you recognize it when it didn't fit the frequency distribution? I believe that's the question.

JEFFRIES: The red area wouldn't be as small. If you put a different isopleth on here -- let's suppose I start with a standard Dodge isopleth; what would the initial frequency distribution in the standard Dodge isopleth look like? Its peak would be shifted upwards. There would be a huge difference between the predicted distribution from the Dodge isopleth and the observed distribution. So the method continues to modify the isopleth until the two converge.

TRIJONIS: At how many points do you measure the difference between the two distributions?

JEFFRIES: Every single point.

TRIJONIS: No.

JEFFRIES: Twenty-eight difference places.

TRIJONIS: How many peak parameters?

JEFFRIES: Seven.

TRIJONIS: Then there could be an overfitting. In fact, I would think there would be an overfitting problem. That's why it fits those points.

JEFFRIES: It's not like we're distorting an isopleth to get the fit.

TRIJONIS: I don't quite agree. The difference in the end is small, but, in your final output, there is an overfitting problem with fitting 7 variables to 28 points.

JEFFRIES: We constrain those points and they can't take on just any values. We constrain the points to take on only values that are very similar to values predicted by the chemical mechanism.

TRIJONIS: That's why I said there's not much difference at the end.

JEFFRIES: The parameters don't change very much. The most critical parameter is the meteorology dilution factor. That's the biggest difference between standard Dodge for Los Angeles with small mixing height rise and St. Louis. So you make half the O_3 for the same starting material. In effect, you could simply take the Dodge isopleth, multiply all the answers by half, all the isopleth numbers by half, and get approximately the same result.

DODGE: When you vary these parameters, are you by any chance altering the chemistry in the sense that, if there are different chemical mechanisms that give different predictions, these differences may be dampened by the iterative process? Does it make the chemistry you start out with less critical?

JEFFRIES: Yes, it does. I can take the final parameters that cause the fit and go back to the mechanisms and see what kinds of things would have had to have been true for certain mechanisms to give a surface that looked like this. The first thing that would have to be true is the dilution has to be bigger than it is in the standard case. The second thing is, the reactivity may be slightly different than it was in the standard case, because reactivity determines the position of the ridge line. So the higher the reactivity, the larger the angle; the more the ridge line moves over. So if the fit had to have a higher or a lower angle, that means that the reactivity of the mix was higher or lower, or the light intensity was larger or smaller. If the curvature is different, it means that the competition between the aldehydes and the apparent HC's for OH was different in that mechanism than in some other mechanism.

So the parameters have specific things in the chemical mechanisms that control their values. I know that because I can change those things in the mechanism; in brief, do an isopleth and refit it and then see the value of the parameters that came out of that change. We have done this. I have many slides here that show all the things that changed in the chemistry, how the isopleth changed, how the parameters changed, and so on. It's not like the parameters are just numbers out of nowhere. They have a physical meaning in terms of the chemistry and the meteorology, the conditions used to solve for the O_3 in the first place.

DIMITRIADES: Would Drs. Trijonis, Whitten and Killus briefly summarize their comments, objections, or reservations for the benefit of the report?

TRIJONIS: I'm not sure it would affect the end predictions at all, but just on a statistical basis I was concerned about the fact that in choosing the seven free parameters, Dr. Jeffries seemed to be fitting an abnormal distribution or a set of random fluctuations in the frequency distribution. It just so happened for this set of data that fewer points fell between 9 and 10 a.m. than between 8 and 9 a.m. or between 10 and 11 a.m. It concerned me that the method selected one of the seven free parameters to fit that abnormality in the 28 data points. I don't think it probably affects the end result. But it's just the statistical question of overfitting to whatever deviations happened to be in this data set.

WHITTEN: I had three questions. One question was that the hour that seemed to be the most important seemed to be the earliest hour chosen, and I would feel more comfortable if that were a peak in a distribution of hours. I would suggest looking at other hours. A second question was about the reality of the model. Is it possible to relate the wind direction on the days where the HC and NO_x pair indicated high O_3? Was the wind blowing in a direction such that that station and that particular pair was at least in the direction of where the maximum was that day? Finally, it's difficult for me to believe that this methodology relates the control of emissions to the reduction of O_3 in the atmosphere. I can see that we have a statistical distribution of NO_x and a statistical distribution of O_3, but it's not necessarily putting a cause and effect relationship between reducing the concentrations of one or the other and reducing the O_3.

JEFFRIES: The point that we used 6 a.m. as the first value (and 6 a.m. is the most frequent concentration period) is valid. We should have looked at 5 a.m. and we didn't. However, my intuition from remembering what the data looks like tells me that 6 a.m. is probably the hour of peak concentration, and that's what the method tends to zero in on, peak concentration.

Concerning wind direction, the model in no way attempts to relate concentration on a given day with O_3 produced on that day. So it doesn't matter where the wind was blowing. The issue is statistical probability that the parcel that you hold in the morning is the parcel that you measure in the afternoon. We are interested in knowing the frequency of occurrence of a HC-NO_x pair and the frequency of occurrence of an O_3 value. That is what the model deals with. For that reason there is no physical cause and effect that I can point to and say, yes, the air flowed from here to there and, yes, it made that O_3. All I can say is that when you put the measurements onto the model dry surface you get the answers that agree with the measured values.

As far as the ability of the model to work in the future under changed conditions, it's like any other particular model: it's tied to the data base that you use. So if something like O_3 aloft is significant today and it is not significant tomorrow, then you're out of luck.

ALTSHULLER: Did I understand that you picked 3 models in each of the 3 years?

JEFFRIES: Four.

ALTSHULLER: Four, okay. Would looking at different time intervals -- 2 months, 4 months, 6 months -- aid in answering some of these other questions that have come up?

WALKER: You said that HC abatement seemed the preferred control strategy, but the distribution of points in your before and after plots does not seem to support that. What do you mean when you say the points slip up and so forth, and work against you on the NO_x values? Superficially, it would seem that NO_x abatement would pull you down into the compliance region faster.

JEFFRIES: That's not true when you actually do the calculation on the surface. The model always tends to choose that precursor pair that is closest to the ridge line. In the future, when you apply as much as 80% HC control, most of the points that you were concerned with now are so NO_x-limited that they don't contribute anything at all to the O_3 production that you're interested in. It was points that had higher HC before but lower NO_x that didn't make the O_3, they weren't the high O_3 pairs today but in the future they will be. Thus the method already has a built-in selection to go to lower NO_x anyway, and the fact that you reduce NO_x doesn't change things very much.

When you deal with an entire distribution, the issue is this: NO_x control is unusual in that on one side of the diagram it helps you but on the other side of the diagram it hurts you. Hydrocarbon control either leaves things the same or reduces the O_3, and what happens is that the distributions are such that there is good probability that reducing NO_x only will help you in some cases and hurt you in some cases, and those tend to offset each other. However, HC control almost always either doesn't change anything or helps you. You have to deal with the entire distribution and if you don't, you're not looking at the whole problem.

KILLUS: Suppose you were to take a HC and NO_x distribution in some completely different city, or perhaps a random HC and NO_x distribution, and started running that through your model, fitting it to the O_3. I believe if that then failed, you'd have a reasonable test of your model. If, however, it succeeded, you obviously have spurious data.

JEFFRIES: It's obvious it will fail. Suppose it were a uniformly random distribution; then every O_3 concentration is equally like that.

KILLUS: No, not the O_3 concentration. I'm talking about HC and NO_x precursors. Assume you take a random HC and NO_x precursor set and the real St. Louis O_3 set, and try to see if you can regularize the two. If you feed that through your model and you still get the same sort of frequency distribution of O_3, you certainly haven't discovered a relationship between HC and NO_x to O_3. The same is true if you were to take a HC:NO_x ratio from a completely different city. Essentially what I'm asking is whether there is any way of assuring that the HC and NO_x distribution in St. Louis really reproduces the O_3 in St. Louis?

JEFFRIES: What makes the O_3 in St. Louis? Hydrocarbons in Los Angeles? No, clearly.

KILLUS: Exactly. If your model can reproduce the O_3 distribution for HC and NO_x data somewhere else, obviously then the model is incorrect. However, if the model fails under those circumstances, then I believe our concerns about spurious data are somewhat alleviated. Would that be a reasonable test?

TRIJONIS: It might be. I'm not sure the end results are affected by it. I just know that fitting a 7-parameter model with 28 data points shouldn't be done.

JEFFRIES: If I had done what Post did, that is, take the Dodge isopleth, plot these points on it and conclude that multiplying the Dodge isopleths by 1/2 yields the right O_3 values, I wouldn't be fitting anything.

BUFALINI: Haven't you answered the question by saying that, when applied to Sydney, Australia, those factors were a little bit different?

JEFFRIES: Yes. The factors are city-specific.

BUFALINI: Therefore, doesn't that answer the question?

KILLUS: Not if the HC and NO_x distribution in Sydney, Australia happen to be the same as the HC and NO_x distribution in St. Louis.

JEFFRIES: If you took the HC and NO_x distribution I had and shifted all the points a little bit, it's very clear you get a different frequency distribution predicted by the model. I did that. That's how I did the control calculations. So it's very clear that any juggling of the HC-NO_x distribution is reflected instantly in the O_3 frequency distribution predicted by the system. Any modification of the precursor distribution gives rise to a different frequency distribution. What I have done is to find the set of parameters that most closely relates to standard mechanisms in a smog chamber and which also gives the frequency. Taking the precursor distributions and putting them on that surface gives rise to the O_3 distribution.

KILLUS: If you took your shifted HC and NO_x with control and then renormalized your isopleth diagram through your fitting procedure, would you not then again reproduce your present O_3 frequency distribution? Would you get a different isopleth diagram, for example?

JEFFRIES: What do you mean by "renormalize"?

KILLUS: I mean refit your O_3 isopleth; the shifting of a frequency distribution on an isopleth diagram that has been designed to transform a HC and NO_x frequency distribution into an O_3 frequency distribution is not the same as comparing whether one can generate an arbitrary transfer function in the HC:NO_x ratios or HC and NO_x distribution and the O_3 distribution and always get the frequency distribution. If you can always get your frequency distribution of O_3 from any HC and NO_x distribution, then you don't have a predictive model.

ESCHENROEDER: The result is right there. It gives a different O_3 frequency distribution.

KILLUS: No, it gives a different O_3 frequency distribution with the same O_3 isopleth that originally transferred one HC and NO_x distribution to another. I am asking whether any arbitrary isopleth diagram can be so constructed.

ESCHENROEDER: You're saying old O_3 frequency with the new $HC:NO_x$ data?

KILLUS: Yes.

ESCHENROEDER: That is not going to work. The new data gave a new result, as we already saw. Am I correct?

JEFFRIES: Yes, sir.

ROMANOVSKY: You raised a very controversial practical issue here. Before someone reports to Congress that the control of NO_x would not be cost effective, I think we need to remember that there are other environmental problems associated with this photochemical system. Have you looked at other environmental pollutants, I suspect not nitric acid, but hopefully NO_2, in the same light?

JEFFRIES: My comment was specifically addressed to whether control of NO_x in this model was of benefit in terms of controlling the O_3. That's all I can say. And I haven't looked at anything else.

4. SIMPLIFIED TRAJECTORY ANALYSIS APPROACH FOR EVALUATING THE OZONE ISOPLETH PLOTTING PACKAGE/EMPIRICAL KINETIC MODELING APPROACH

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ABSTRACT

The ability of the trajectory model underlying the Empirical Kinetic Modeling Approach (EKMA) to predict peak ozone concentrations was examined. Detailed air quality, emissions, and meteorological information available from the St. Louis Regional Air Pollution Study was used as input. In addition, sensitivity of model predictions to varying morning and afternoon mixing heights input to the model and varying spatial detail in emissions input were investigated.

Results indicate that the model tends to underpredict peak ozone observed in St. Louis. However, of the ten cases examined, six agreed with observed peaks within ± 30% for at least part of the range of input variables examined. The four cases, for which poor agreement between observations was always obtained, were examined to ascertain reasons for the lack of agreement. It was concluded that the poor agreement probably arises primarily from incorrect input to the model (e.g., incorrect trajectories, inaccurate mixing height profiles, etc.). Since the Regional Air Pollution Study data base is likely to be superior to data bases for most other cities, similar difficulties may be encountered elsewhere.

INTRODUCTION

The Empirical Kinetic Modeling Approach (EKMA) is a procedure developed by the U.S. Environmental Protection Agency (EPA) to estimate the reductions in precursor emissions necessary to achieve the National Ambient Air Quality Standard (NAAQS) for ozone (O_3) (Gipson et al., 1981; Federal Register, 1981). The approach uses an O_3 isopleth diagram which presents peak hourly-average O_3 concentrations explicitly as a function of early morning precursor levels. The positioning of the isopleths is an implicit function of a number of other factors as well (e.g., meteorology, emissions, and transported pollutants). The diagrams are developed using the Ozone Isopleth Plotting Package (OZIPP), which incorporates a simplified trajectory model (Whitten and Hogo, 1978; EPA, 1978).

The objective of this study was to investigate one approach for assessing the validity of the EKMA procedure. This approach attempts to assess how accurately the model used to generate the EKMA isopleths is able to predict peak O_3 concentrations using detailed input information. Such an approach does not directly answer the key question of how accurately the model predicts changes in peak O_3 accompanying a reduction in precursors. However, successful prediction of base-case conditions provides some confidence that the model provides a reasonable approximation of physical and chemical phenomena. Further, if the model can predict base-case conditions accurately in several cities with varying levels of precursors, one may place additional confidence in the predicted controls.

This report provides an overview of the study, a brief explanation of the trajectory model contained in OZIPP, and a description of the data base employed in the study. It also describes the methodologies employed to derive the information necessary to apply the model to the urban area under study and discusses the results of the model application.

Background

The EKMA procedure uses the trajectory model contained in OZIPP to express maximum hourly average O_3 concentrations as a function of early morning ambient levels of nonmethane organic compounds (NMOC) and total oxides of nitrogen (NO_x). The functional relationship derived using the trajectory model takes the form of an O_3 isopleth diagram. An isopleth diagram can be tailored to a specific area or situation using city-specific information on emissions, transport, and dilution. The diagram is designed to be used with a measured peak hourly O_3 concentration and morning NMOC:NO_x ratio to estimate the reductions in emissions necessary to achieve the NAAQS for O_3.

The approach used in this evaluation of EKMA was to employ atmospheric data to test the trajectory model used to develop the isopleth diagrams. That is, measured ambient O_3 peaks were compared to peak levels of O_3 predicted by the trajectory model. In the analysis described in this report, the model was applied to the St. Louis metropolitan area, for which an extensive air quality, meteorological, and emissions data base was compiled under the

Regional Air Pollution Study (RAPS). This data base contained sufficient information to evaluate the performance of the trajectory model in predicting peak O_3 concentrations, to investigate other facets of model performance, and to examine potential problem areas in the model's absolute prediction capabilities.

Description of Trajectory Model and Its Application

The conceptual basis for the trajectory model in OZIPP is similar to a Lagrangian photochemical simulation model (Figure 4-1). A column of air is advected by the wind along a specified trajectory. The height of the column is equal to the mixing depth (i.e., the column extends from the earth's surface through the mixed layer). Horizontal dimensions are selected such that concentration gradients are small, and thus the effects of horizontal exchange of air between the column and its surroundings can be ignored. Within the column, air is assumed to be uniformly mixed at all times.

Initially, the column contains predetermined levels of pollutants (primarily NMOC and NO_x), which may result from prior emissions and/or possible transport from upwind areas. As the column moves along the trajectory, its height increases with the diurnal rise in mixing height. As the mixed layer grows, air above the column mixes downward into the column instantaneously, leading to the entrainment of additional pollutants found above the early morning mixed layer. Also, the column moving along the trajectory can encounter fresh emissions of precursors, further adding to

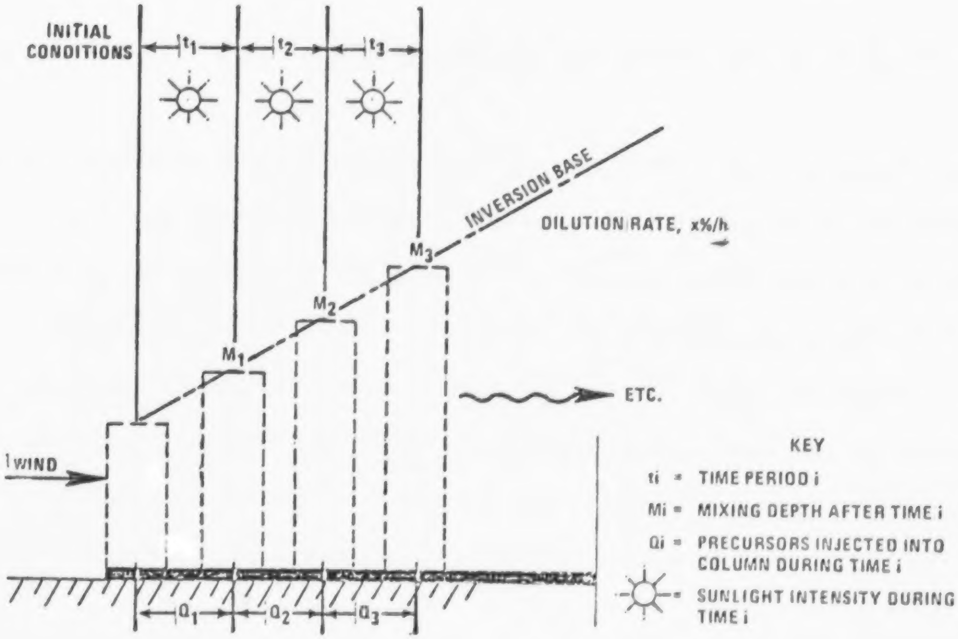

INITIAL CONDITIONS
t1
t2
t3
INVERSION BASE
DILUTION RATE, x%/h
M1
M2
M3
ETC.
WIND
Q1
Q2
Q3
KEY
ti = TIME PERIOD i
Mi = MIXING DEPTH AFTER TIME i
Qi = PRECURSORS INJECTED INTO COLUMN DURING TIME i
SUNLIGHT INTENSITY DURING TIME i

Figure 4-1. Conceptual view of trajectory model in OZIPP.

pollutant concentrations. Consequently, pollutant concentrations within the column are physically increased by emissions and entrainment of pollutants from aloft, and decreased by the increase in volume of the column caused by the rise in mixing height (i.e., dilution).

The trajectory model mathematically simulates the changes in pollutant concentrations that result from the physical processes described above and from chemical reactions taking place within the column. A chemical kinetic mechanism incorporated into the model mathematically describes these chemical reactions. For those reactions affected by sunlight, the rates of reaction are estimated by theoretical considerations of diurnal variation in solar radiation. The trajectory model calculates the concentrations of all reactive species included in the chemical mechanism as a function of time. In addition, the model determines the maximum 1-h average O_3 concentration occurring during the simulation. This peak O_3 concentration, therefore, is a function of the following factors:

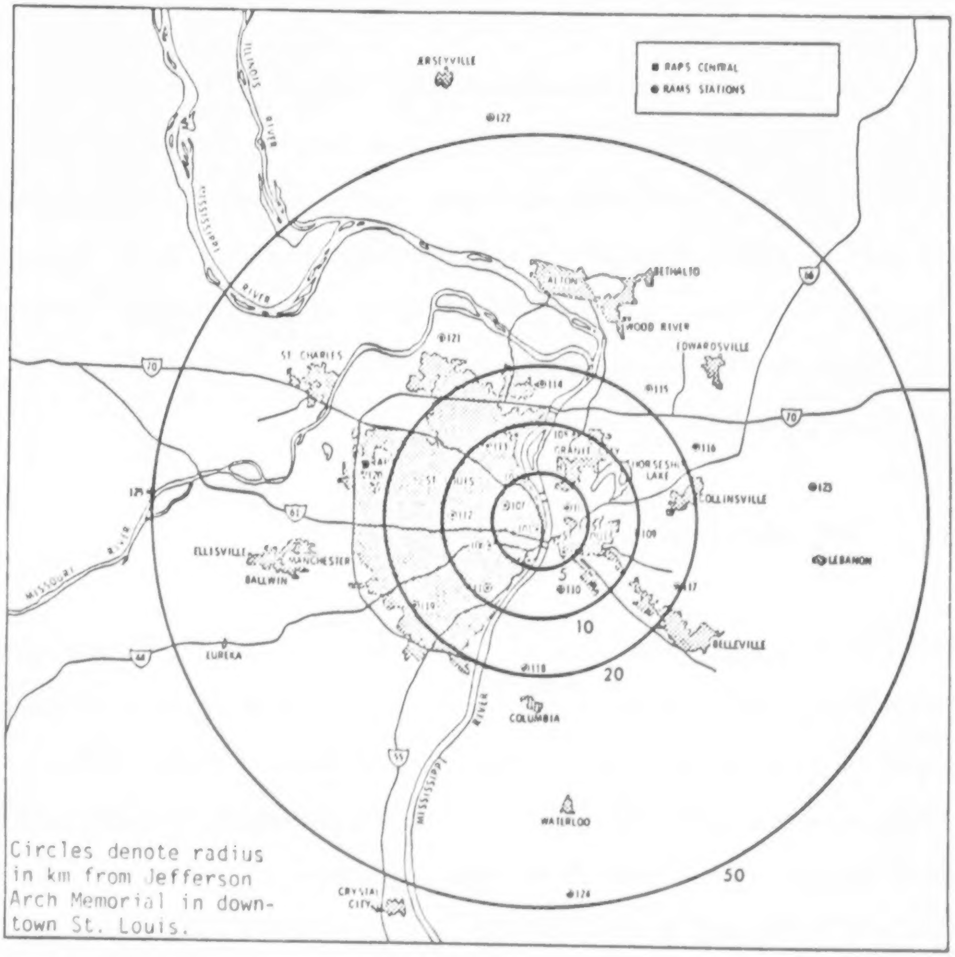
- initial pollutant concentrations
- emissions occurring along the trajectory
- dilution of pollutants caused by rise in mixing height
- entrainment of pollutants from aloft
- chemical reactions affecting pollutant concentrations

RAPS Data Base

An extensive air quality management data base was compiled under RAPS. This data base contains all the elements necessary to evaluate air quality simulation models, including air quality, emissions, and meteorological data sufficiently resolved in space and time to develop input data and provide measures for evaluating model performance. The data base as it relates to this study is briefly described below.

The bulk of the air quality data used in the study was collected at 25 regional air monitoring stations (RAMS) spaced concentrically throughout the study region (Figure 4-2). These stations were located such that they would not be unduly influenced by any one source or group of pollutant sources. At each station, hourly average concentrations for the following pollutants were recorded: O_3, nitrogen dioxide (NO_2), nitric oxide (NO), NO_x, NMOC, and carbon monoxide (CO). The size of the network, quality of data, and duration of measurements provide the best available temporal and spatial resolution of ambient pollutant levels available to evaluate a model such as the trajectory model incorporated within OZIPP.

The emissions data employed in this study included an hourly resolved area- and point-source emissions inventory for NO_x, CO, and reactive hydrocarbons (RHC's). The area-source emissions were spatially resolved by means of the RAPS grid system, which consists of about 2000 variably sized grids (Hans and Paddock, 1975). Thus, estimates of emissions rates from both


RAPS CENTRAL
RAMS STATIONS
JERSEYVILLE
122
ILLINOIS RIVER
MISSISSIPPI RIVER
ALTON
BETHALTO
WOOD RIVER
EDWARDSVILLE
121
ST. CHARLES
70
114
115
GRANITE CITY
HORSESHOE LAKE
116
ST. LOUIS
111
120
125
61
112
107
COLLINSVILLE
123
109
ELLISVILLE
MANCHESTER
BALLWIN
MISSOURI RIVER
LEBANON
5
110
117
119
10
BELLEVILLE
44
EUREKA
118
20
COLUMBIA
55
MISSISSIPPI RIVER
WATERLOO
50
124
CRYSTAL CITY

Circles denote radius in km from Jefferson Arch Memorial in downtown St. Louis.

Figure 4-2. RAMS station locations.

area and point sources are available by hour and by grid for any day in 1975 and 1976, the primary period covered by RAPS.

The primary source of meteorological data consisted of continuous measurements of wind speed, wind direction, and temperature made at each of the 25 RAMS stations. Additional data were collected from the RAPS Upper Air Sounding Network (UASN). In this program, radiosondes were conducted three times per day, five times per week, at a minimum of two stations. From these soundings, vertical temperature profiles are available from which mixing heights can be estimated.

METHODOLOGY FOR DEVELOPMENT OF MODELING DATA

We chose 10 trajectories on 9 different days during 1976 to evaluate the trajectory model's performance in the prediction of peak O_3 concentrations. We employed several criteria in the selection of days. Because EKMA is necessarily used for those days with the highest O_3 levels, primary interest focused on predicting the highest O_3 levels measured in the region. Further, we selected a sufficient number of days to insure that the model's performance be evaluated for a number of different atmospheric conditions. We included a few days with lower O_3 concentrations to test for a possible systematic bias in the model's predictions. These considerations led to the selection of the 10 test cases summarized in Table 4-1.

TABLE 4-1. MODEL TEST CASES

Date	Julian Date	RAMS Site	Time of Peak O_3 (LDT)*	Peak O_3 Concentration (ppm)
10/01/76	275	102	3:00-4:00 p.m.	0.24
07/13/76	195	114	4:00-5:00 p.m.	0.22
06/08/76	160	115	5:00-6:00 p.m.	0.22
06/07/76	159	122	4:00-5:00 p.m.	0.20
06/08/76	160	103	2:00-3:00 p.m.	0.19
08/25/76	238	115	2:00-3:00 p.m.	0.19
10/02/76	276	115	5:00-6:00 p.m.	0.19
09/17/76	261	118	1:00-2:00 p.m.	0.15
07/19/76	201	122	1:00-2:00 p.m.	0.15
08/08/76	221	125	6:00-7:00 p.m.	0.12

*Local daylight time.

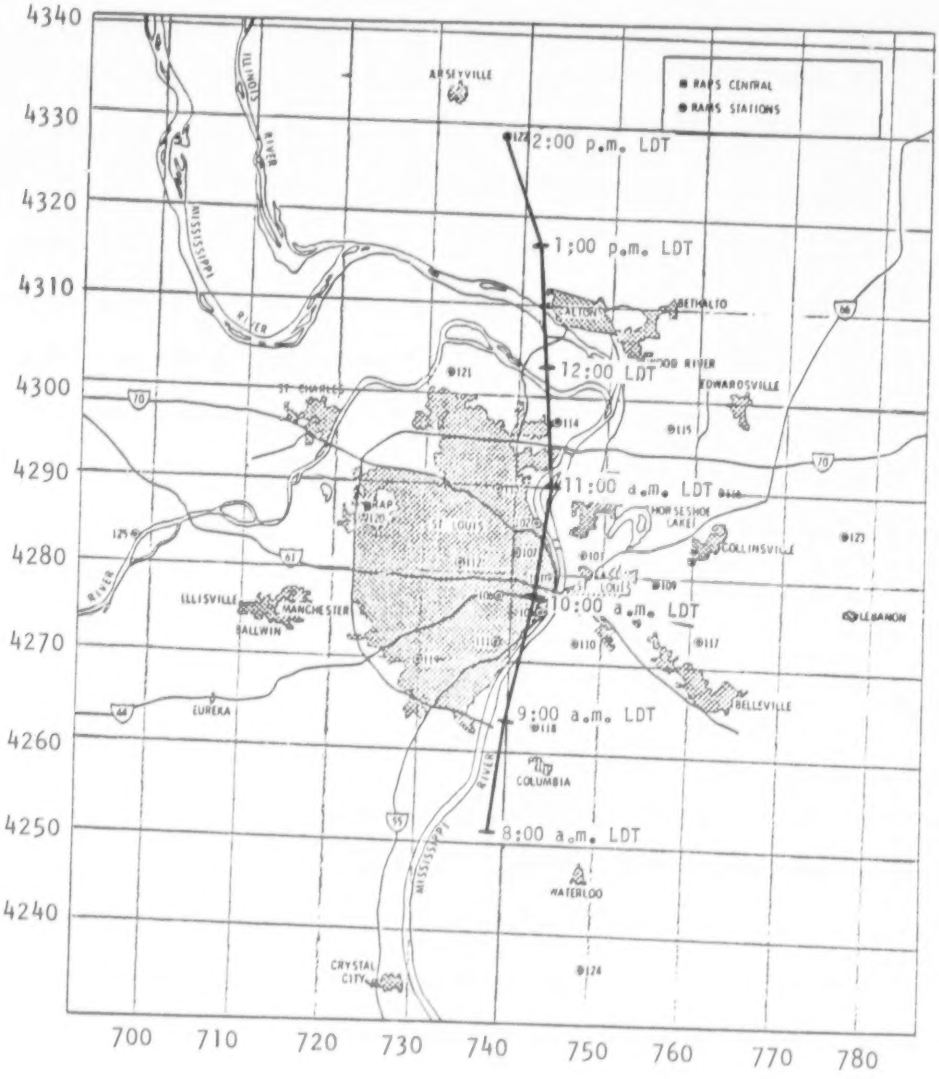
The first step in performing an air quality simulation involves deriving an air-parcel trajectory corresponding to the time and location of the observed peak O_3 concentration. This trajectory represents the path an air parcel would have traveled to reach the site of interest at the specified time (thereby representing the movement of the theoretical column previously described). Once the column movement is defined, the remaining information necessary to simulate a test case can then be developed, that is, the initial conditions, emissions, boundary conditions (O_3 aloft), and dilution data needed. The following section describes the methodologies we used to develop each of these.

Air Parcel Trajectory

We calculated air-parcel trajectories for each of the test cases from the minute-by-minute measurements of wind speed and wind direction taken at each of the 25 RAMS stations. First, we calculated 10-min vector averages of wind speed and direction for each of the 25 sites. We then averaged the individual site averages to obtain an overall regional average wind speed and direction for each 10-min period. We could then use the regional average wind speed and direction to track a trajectory backwards from the site and time of the observed peak O_3 concentration until 8:00 a.m. Central Daylight Time (CDT). Figure 4-3 illustrates the back trajectory for the July 19 test case, with the hourly segments of the trajectory shown along the path.

Initial Concentrations

The initial concentrations of NMOC, NO_x, and O_3 represent the pollutant levels that were initially within the theoretical model column at 8:00 a.m. CDT. They were estimated from the hourly averaged concentrations at the RAMS stations nearest the trajectory starting point. The first step in the procedure was to select the three RAMS sites closest to the trajectory starting point. For these three sites, we computed instantaneous concentrations corresponding to the simulation starting time by averaging the


4340
4330
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4300
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4280
4270
4260
4250
4240
700
710
720
730
740
750
760
770
780
RAPS CENTRAL
RAMS STATIONS
2:00 p.m. LDT
1:00 p.m. LDT
12:00 LDT
11:00 a.m. LDT
10:00 a.m. LDT
9:00 a.m. LDT
8:00 a.m. LDT
ARSEYVILLE
ILLINOIS RIVER
MISSISSIPPI RIVER
ALTON
BETHALTO
WOOD RIVER
EDWARDSVILLE
ST CHARLES
ST LOUIS
HORSESHOE LAKE
COLLINSVILLE
LEBANON
ELLISVILLE
MANCHESTER
BALLWIN
EUREKA
BELLEVILLE
COLUMBIA
WATERLOO
CRYSTAL CITY
70
61
44
55
66

Figure 4-3. Air-parcel trajectory for July 19 test case.

hourly pollutant levels for the hour immediately preceding the starting time and the hour immediately following the starting time. For example, we would calculate the 8:00 a.m. CDT instantaneous concentration for a pollutant at one site by averaging the 7:00 a.m. to 8:00 a.m. and the 8:00 a.m. to 9:00 a.m. hourly levels. We then computed the initial column concentrations as a weighted average of the three instantaneous levels, with the weighting factors equal to the square of the reciprocal of the distance between each RAMS site and the trajectory starting point (i.e, $^1/r^2$). In performing these calculations, we set any concentration below the minimum detectable limit of the analyzer equal to the following lower limits: 0.005 ppm for NO_x; 0.1 ppmC for NMOC; and 0.005 ppm for O_3.

Emissions

As previously mentioned, the trajectory model also simulates the impact of precursor emissions occurring after the simulation starting time. Therefore, we also used hourly emissions rates for NMOC and NO_x. The emissions encountered by the column during each hour are input to the model as fractions of initial concentration of NMOC or NO_x. We computed the fractions themselves by comparing the emissions densities encountered by the column of air during each hour to the pollutant density initially in the column.

From the RAPS emissions inventory, an average emissions density for each hour of the column trajectory path could be computed. We did this by (1) summing the hourly point- and area-source emissions occurring within each grid square encountered by a trajectory segment, (2) dividing the total emissions in each grid square by the area of that grid square, and (3) weighting the resulting emissions densities consistently with the proportion of the trajectory segment in each grid square. For example, consider the trajectory path shown in Figure 4-4. An emissions density for the first hour (i.e., 8:00 a.m. to 9:00 a.m. LDT) would be calculated from the total emissions occurring between 8:00 a.m. and 9:00 a.m. LDT within grid squares (1) and (2). Since roughly two-thirds of the trajectory segment between 8:00 a.m. and 9:00 a.m. occurs in grid square (2), the emissions density in (2) is weighted by a factor of 0.67, whereas the emissions density in grid square (1) is weighted by a factor of 0.33.

We calculated the actual fractions input to the OZIPP model for both organic compounds and NO_x using the following expressions:

$$e_i = \frac{Qi}{Ho\ Co\ \rho} \qquad (4\text{-}1)$$

where: e_i = fraction of initial concentration to be added during hour i to represent emissions occurring during hour i

Qi = emissions density for hour i (mol/m^2)

Ho = initial morning mixing height as described previously (m)

Co = initial pollutant concentration (ppm or ppmC)

ρ = density of air (41 mol/m^3)

Equation 4-1 represents the ratio of the emissions density at a particular

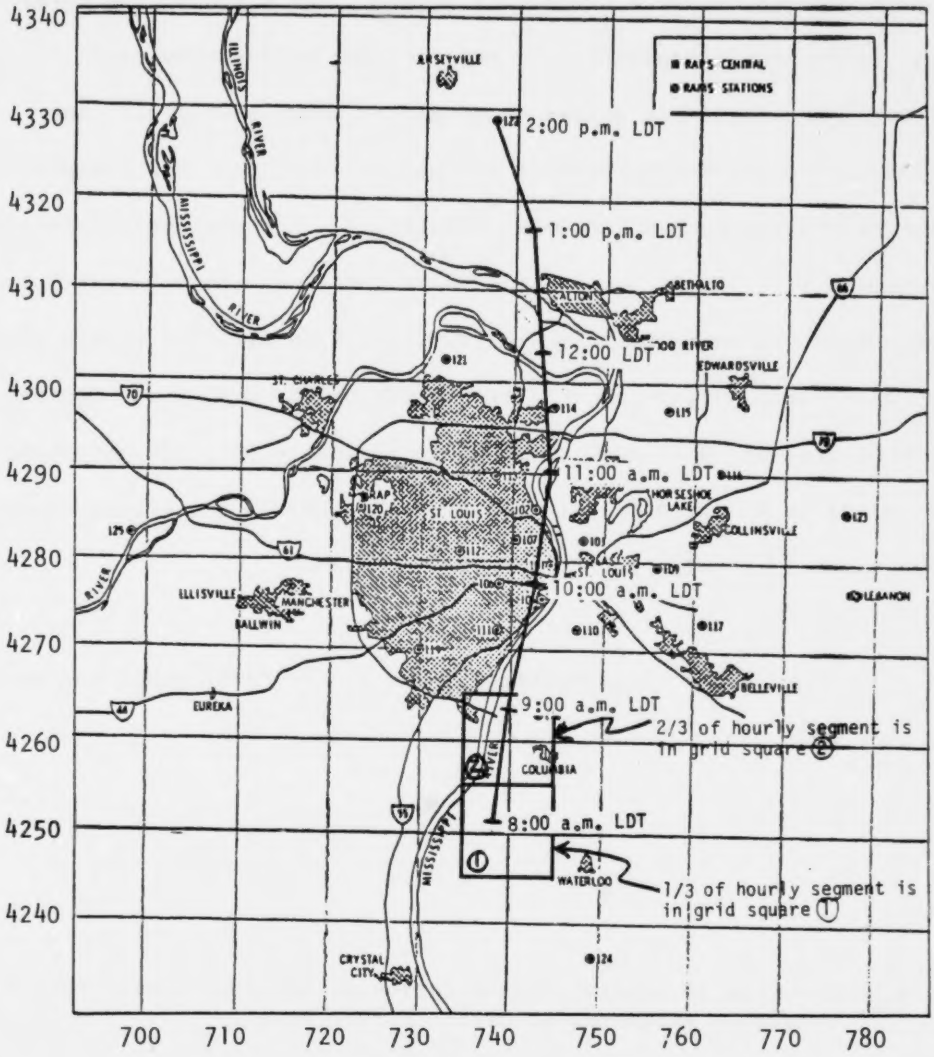
4340
4330
4320
4310
4300
4290
4280
4270
4260
4250
4240
700
710
720
730
740
750
760
770
780
RAPS CENTRAL
RAPS STATIONS
JERSEYVILLE
ILLINOIS RIVER
MISSISSIPPI RIVER
2:00 p.m. LDT
1:00 p.m. LDT
12:00 LDT
11:00 a.m. LDT
10:00 a.m. LDT
9:00 a.m. LDT
8:00 a.m. LDT
ALTON
BETHALTO
WOOD RIVER
EDWARDSVILLE
ST. CHARLES
70
66
ST. LOUIS
RAP
HORSESHOE LAKE
COLLINSVILLE
61
ELLISVILLE
MANCHESTER
BALLWIN
EAST ST. LOUIS
LEBANON
BELLEVILLE
EUREKA
44
55
COLUMBIA
WATERLOO
CRYSTAL CITY
121
122
114
115
116
113
120
102
107
112
123
125
101
103
109
106
110
111
108
117
124
2/3 of hourly segment is in grid square ②
1/3 of hourly segment is in grid square ①
②
①

Figure 4-4. Air-parcel trajectory for July 19 test case demonstrating how fresh precursor emissions are considered.

hour to a hypothetical column density based on the initial column conditions. In the above expression, the area of the column does not appear. However, the emissions density term, Qi, implicitly accounts for this term. Hence, one can vary the impact of fresh emissions simply by changing the size of the grid squares used in the modeling exercise. As subsequently described, we performed model sensitivity tests to grid-square size.

Emissions derived from the RAPS inventory were expressed on a mass basis (e.g., kg). To convert to a molar (or ppm) basis, we used the following conversion factors: 46 g/mol for NO_x and 14.5 for NMOC. For NO_x, the inventory gives NO_x as equivalent NO_2, and for NMOC, 1.0 ppmC is assumed equivalent to $CH_{2.5}$.

Boundary Conditions

Boundary conditions for the trajectory model include pollutant concentrations found in the layer above the early morning mixed layer. Gipson et al. (1981) have described the procedure used to estimate the level of O_3 aloft. We averaged hourly O_3 concentrations measured between 11:00 a.m. and 1:00 p.m. CDT at upwind, rural-type monitors to obtain an estimate of the levels aloft (Table 4-2 summarizes the results). We assumed any precursor pollutants aloft to be negligible.

TABLE 4-2. ESTIMATES IN O_3 ALOFT

Date	Julian Day	O_3 Aloft (ppm)
10/01/76	275	0.06
07/13/76	195	0.08
06/08/76	160	0.10
06/07/76	159	0.11
08/25/76	238	0.09
10/02/76	276	0.06
09/17/76	261	0.06
07/19/76	201	0.08
08/08/76	221	0.07

Dilution

Dilution in the trajectory model results from the change in mixing height throughout the day. In the OZIPP model, the mixing height is assumed to rise as a function of the time after sunrise in accordance with a "characteristic curve." This so-called characteristic curve has been derived empirically from data taken during the RAPS study. The curve is defined by specifying the 8:00 a.m. CDT and maximum afternoon mixing heights. We derived these heights using information from soundings taken just prior to sunrise, in mid-morning, and in mid-afternoon. Then we fitted the diurnal mixing height curve between the 8:00 a.m. and maximum afternoon mixing height. The result was an

"S"-shaped curve in which little or no increase in mixing height occurred in the early morning, followed by a large increase in mid-morning, and smaller increases thereafter. Although the shape of the diurnal mixing height curve remained invariant in these tests, the height itself could be manipulated at any time by specifying different 8:00 a.m. and/or maximum afternoon mixing heights. Since there is usually some uncertainty about these morning and afternoon estimates, we examined the model's sensitivity to different values.

Chemical Mechanism

We used the Dodge chemical kinetic mechanism currently incorporated in OZIPP in all 10 tests (Whitten and Hogo, 1978) and employed observed NO_2/NO_x fractions to apportion initial NO_x between NO and NO_2. We used default parameters for all other variables (Gipson et al., 1981).

RESULTS AND DISCUSSION

Figure 4-5 presents the results of the 10 tests. The solid line beginning at the origin represents perfect agreement between observed peak hourly O_3 concentrations (abscissa) and predicted peaks (ordinate). The broken lines on either side of this 45-degree line represent agreement to within ± 30%. The numbers on the graph represent the Julian day corresponding to each of the 10 test cases. The series of vertical lines shown in Figure 4-5 depicts the range within which model predictions varied when mixing

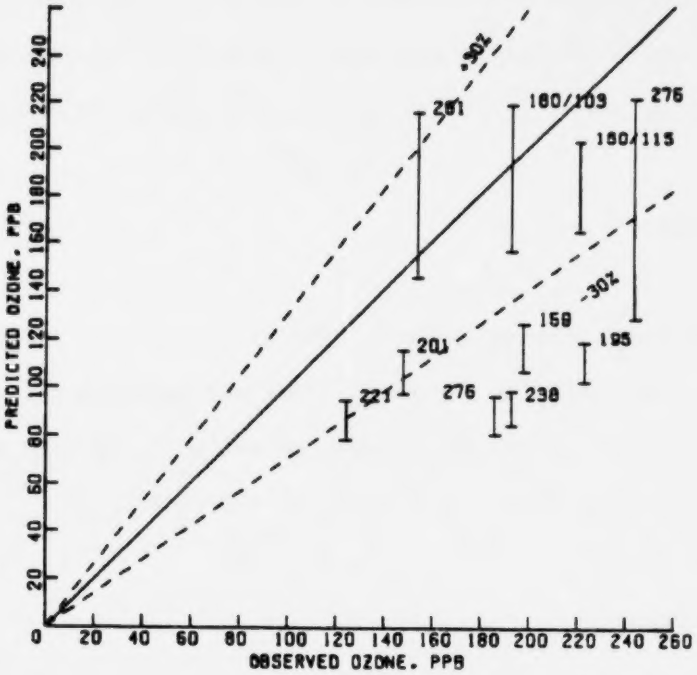

Figure 4-5. Comparison of observed and predicted peak hourly O_3 concentrations.

heights and/or grid-square size were varied. Table 4-3 shows the range over which these three variables were varied for each test case. It is difficult to generalize about the sensitivity of the predicted peak O_3 to the three inputs which were varied. Model sensitivity to these inputs depends to some extent upon factors which were not varied (i.e., initial precursor concentrations and O_3 aloft). Nevertheless, for the sensitivity studies performed, the inputs that were varied could usually be ranked (most sensitive first) as follows:

(1) morning mixing heights
(2) afternoon mixing heights
(3) grid-square size

Referring to Figure 4-5 for 6 of the 10 test cases, predicted peak O_3 agreed to within ± 30% of the observed values, at least over part of the range of sensitivity tests. An apparent tendency exists, however, for the model to underpredict observed peak O_3 levels. Also, no one has yet attempted to compare observed and predicted diurnal precursor concentrations within the column of air. For 4 days (Days 159, 195, 238, and 276), the trajectory model grossly underpredicted observed peak O_3 for all cases. Fxamining these 4 days in further detail reveals several possible explanations for the poor model performance.

First, the derived trajectories may be grossly incorrect. For example, on Day 159, upper-air soundings suggest that the winds tend to veer clockwise

TABLE 4-3. RANGE OF SENSITIVITY TESTS FOR 10 TEST CASES

Case	Julian Day	Grid-Square Size (km)	Sunrise Mixing Height (m)	Maximum Afternoon Mixing Height (m)
1	159	5x5, 10x10, 20x20	90-290	1850-1990
2	160/(103)	5x5, 10x10, 20x20	100-250	1957-2010
3	160/(115)	5x5, 10x10, 20x20	100-250	1957-2010
4	195	5x5, 10x10, 20x20	50	1300-1860
5	201	5x5, 10x10, 20x20	100-250	1500-2310
6	221	5x5, 10x10, 20x20	100-250	1233-1570
7	238	5x5, 10x10, 20x20	100-250	1764
8	261	5x5, 10x10, 20x20	100-250	1720
9	275	5x5, 10x10, 20x20	100-250	530-850
10	276	5x5, 10x10, 20x20	100-250	1800

with increasing altitude within the mixed layer. Therefore, in at least some cases, use of surface winds to derive trajectories may result in inaccurate estimates for trajectories. In the case of Day 159, winds measured above the surface but still within the mixed layer suggest a trajectory that goes through areas of greater precursor emissions. While such corrections may result in better model performance on some days, upper-air data are limited, especially with regard to sampling time. Using such limited data to derive continuous trajectories may also introduce large uncertainties into the trajectory analysis.

Second, in some cases, the methodology employed in the model may be too rigid to allow accurate simulation of key variables. For example, upper-air data taken on Day 195 suggest that the mixing height remains low until mid-to-late morning. This includes a period in which the trajectory passes through an area with a high emissions density. For this day, the characteristic curve computerized fitting scheme results in the mixing height rising too soon, thereby diminishing the impact of these fresh emissions. Thus, a different mixing height growth pattern may be more appropriate for this day.

Third, in some cases, the available information may be inadequate to provide reasonable input to the model. This may occur on Day 276, for example, when there are no upper-air soundings for St. Louis. For Day 276 (a Saturday), routine sounding data from a station almost 100 km from St. Louis had to be used to estimate mixing heights.

The foregoing discussion suggests possible explanations for the lack of agreement between results obtained on many of the days when the model performed poorly. The problems generally center on uncertainties in data or the lack of adequate data. Given the comprehensive nature of the St. Louis RAPS data base, applications of the trajectory model to other cities with less detailed data will more than likely lead to similar problems. In fact, the problems encountered with other cities are likely to be even more extensive than those found in the St. Louis application.

CONCLUSIONS AND RECOMMENDATIONS

This paper has discussed one method for evaluating OZIPP/EKMA. The major advantage of this method is that it attempts to incorporate physical reality to the maximum extent consistent with a simple model. Hence, unlike methods that are statistical or based on comparisons of predicted and observed frequency distributions, application of the model in this manner is more likely to reflect cause-effect relationships. The method does not directly address the question of greatest importance (i.e., how accurately changes in O_3 are predicted). In this respect, it is inferior to comparison with historical trends or with controls predicted by sophisticated models. However, these latter two methods have disadvantages as well. In the case of trend comparisons, uncertainty is associated with historical data, few cities are available where the method can be evaluated, and in these, only small changes in precursor levels have been realized. For comparison with sophisticated models, there is no guarantee that the sophisticated model's control predictions are accurate. Furthermore, if the trajectory model can be made to agree with base-case conditions found in cities with widely varying emissions, some insight into the model's ability to replicate changes in emissions may be possible.

In addition to its inability to address directly the key question of how accurately the impact of controls is simulated, the method described in this paper contains several other disadvantages. The first disadvantage of the method is it requires a detailed data base. Secondly, because of the data limitations, the model is not often likely to be applied using the trajectory analysis approach described here. That is, the model will be most often applied in an EKMA Level III analysis in which a trajectory is chosen such that a city's early morning emissions are directly related to the observed O_3 peak (Gipson et al., 1981). The transferability of these findings to a Level III analysis is uncertain. One possible alternative would be to test the model's ability to predict observed peak O_3 when applied in the Level III mode. Such comparisons have been conducted in St. Louis and Philadelphia. In these comparisons, predictions appear to agree reasonably well with observations (see Appendix 4-1).

The results reported herein are not exceptionally good. The following recommendations are suggested as possibilities for further evaluation of the model.

The existing procedure for developing model inputs may be too rigid, thus, more specific consideration of each day may be warranted.

Estimation of the air-parcel trajectory may be grossly inaccurate in some cases. Other approaches for estimating trajectories need to be investigated. One possible method is to use air quality data in addition to wind data to derive trajectories. This may decrease reliance on uncertain and limited information, and would be similar to the Level III analysis since air quality data are used to establish the trajectories in this approach.

The performance of the simple trajectory model described herein could be compared with more sophisticated trajectory models. Assuming the more sophisticated models perform better, sensitivity tests could be derived to perhaps develop compromises that are less data-intensive than the sophisticated models, but perform better than the simple model.

The simple model needs to be tested with other, updated chemical mechanisms. Mechanisms that are more efficient in producing O_3 may produce better results.

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WORKSHOP COMMENTARY

McRAE: Have you compared the amount of material in the column from the initial conditions to the amount that is injected through emissions?

Related to that, if you can use one of these models to predict what is occurring in the atmosphere, how do you change the initial conditions when you are exercising control strategies?

GIPSON: In some cases, the model predictions obviously will be very sensitive to initial conditions. That is all tied into this trajectory and where the starting point is.

As for changing the initial conditions with regard to control strategy, I think you have to look at where the initial conditions are assumed to come from.

If they are assumed to be locally generated materials, and, in fact, in the control strategy you reduce emissions, then you would make some assessment concerning how the initial conditions, the initial concentrations, might change.

An equally proportionate reduction would be a reasonable assumption.

LLOYD: What did you assume for initial aldehydes? Did you do any sensitivity study on those?

GIPSON: No, this is strictly the Dodge mechanism, using the default chemistry in the OZIPP package.

I think aldehyde was 5%.

McKEE: You may have explained this and I missed it. In your 5-km corridor, did you assume that the air parcel remained 5 km wide and moved along like this and picked up sources, or did you assume that each point source diffused by 10° or 15° and became more diluted and contributed less as time went on to that 5-km corridor?

GIPSON: In this type of model, you assume there is a 5-km corridor, and no diffusion.

JEFFRIES: Point sources are treated like area sources. They are incorporated into the area that you're doing the averaging.

KELLY: It looks like your predicted O_3 was lower than that observed.

In other words, the model underpredicted the O_3. Is that correct?

GIPSON: Yes.

KELLY: Other people have been running the model and have had dilution by a factor of two. Do you have any explanation for that?

GIPSON: They are starting from a standard diagram and diluting it. This, of course, implies that the model is overpredicting. However, those conditions are probably not realistic in the St. Louis situation.

Most of the models that have been applied to St. Louis, I think, have a tendency to underpredict O_3. I think it's not only this one, but also some of the more sophisticated models, though, maybe not to this extent.

KELLY: This is going to have a better estimate of dilution than just the standard?

GIPSON: We are trying to tie the specific meteorology of the day to the observed O_3. With observed O_3, we're trying to model that situation by inputting the best type of information, the best available information we have, even though it's still a simple modeling approach.

DODGE: Mr. Gipson, did you try to validate the meteorology by checking CO levels before you ran the chemistry?

GIPSON: In the original work that we did, we did look at CO levels. However, we have completely revamped our trajectory analysis approach. I haven't done that in this set of --

AUST: We did almost the same thing in the Baltimore area and got the same type of results. We took the EKMA model and then fell back to all the default values, using the center-city atmospheric effects. We got essentially good correlation.

Did you get that here? Why wasn't there better correlation here?

GIPSON: Yes, we did it for St. Louis, and we got a much better correlation.

I think the answer is very simple. We're starting off in the urban corridor with high initial concentrations, and in that type of trajectory model, you're going to be able to form more O_3.

I think the one thing you might want to consider with this air-parcel-type approach is that when you start off in the city, the air parcel with high initial concentrations is going to go downwind.

It may miss the monitoring site slightly, but --

AUST: I understand the mechanics of it. Is this part of the analogy of the model itself or should we be working with the trajectory at all, using this particular model?

GIPSON: Well, I have some reservations about deriving trajectories from surface wind measurements. I think there are problems in that.

I don't think some of the problems with underprediction will ever be solved by substituting a different mechanism. There are some trajectories that simply miss the entire city, completely. That is a problem.

KILLUS: How does the amount of dilution in these runs compare with the amount in the standard-EKMA model? Are these much greater dilutions?

GIPSON: That is hard to explain. We have to go back to the standard EKMA and talk about an exponential growth. The standard EKMA is about 3%. These are comparable, I think, to about 23%, 23 or 24%. But we changed the mix in our profiles.

JEFFRIES: The same delta occurs, but it's distributed in time differently.

The standard EKMA model gives you a constant dilution rate.

KILLUS: This wasn't then city-specific EKMA using day-specific mixing?

JEFFRIES: No, it's the same profile. The same profile is used, but day-specific initial and final input numbers are used. Overall dilution is exactly the same, theoretically, as what would occur, but the time of occurrence has been moved around.

Thus, there's less dilution in the morning, more dilution at midday, and less dilution in the evening.

But he [Mr. Gipson] would put a straight line through what's the sigmoid shape of this one.

WHITTEN: I'd like to address two points. One is that some of the more updated versions of chemistry tend to make more O_3 from the same amount of precursors, which would tend to bring your points further up.

In fact, the Dodge chemistry results, explained in my talk, can be modified with just one small change, which would produce the same effect.

The second point I want to address is that an EKMA version we've been preparing for the South Coast District to use in their SIP's has trajectories that go up to 30 h in time. We had to address this problem of a 5-km box maintaining its size.

What we were coming up with was a kind of reverse funnel, in that the trajectory started out being very wide and ended up being very narrow.

What this addresses is an averaging of the emissions density. Thirty hours earlier you may have taken an emissions density over a wide area and averaged all of the emissions. As you come closer and closer to the trajectory's destiny, the averaging area narrows, so that the local emissions become the only ones that it influences.

This is an approach that we've taken. It's actually the opposite of what you're saying.

JEFFRIES: It is true, as Dr. Whitten said, that the newer mechanisms are more reactive for a given amount of precursor material.

They are also more sensitive to the initial source of radicals and to aldehydes. Lots of things average out between the Dodge and default mechanisms and the newer mechanisms that supposedly represent events that need more data.

So changing the mechanism often leads to worse predictions because you don't know the inputs that those new mechanisms need. If you believe the numbers that you have, you may end up predicting lower values.

So there is a trade-off in terms of where the uncertainty is.

WHITTEN: Part of that is coming from the fact that the original mechanism has a default --

JEFFRIES: Right.

WHITTEN: Newer mechanisms are now getting there.

JEFFRIES: I think one has to be very careful when you're talking about the Dodge mechanism.

When you're talking about the Dodge mechanism in a case like this and OZIPP, you must carry with that an enormous range of standard default assumptions and conditions like the 25% to 75%, the 5%, and so forth.

In the newer mechanisms, all those things are adjustable.

Whereas with Dodge, you want to hold all of those constant because any change in them means the original validation work doesn't hold up.

So when you talk about Dodge, you're also talking about several default values that aren't modified in a case like this.

TRIJONIS: What do you think is the most likely reason for the underestimation? Have you given that much thought?

GIPSON: Well, I think there are different considerations on different days. There's no one single cause.

For example, on Day 238, when there was significant underprediction, the trajectory just missed the whole city. There's nothing that you're going to be able to do to make it work. That says something about the control-strategy design. You can control in the rural areas. I just don't believe the trajectory is telling us where the O_3 is coming from.

You know, it's an error in the input data, basically, or the assumptions of the simple type model don't hold up under this particular situation.

For some of the other days, I think maybe the results could be improved. It looks like the characteristic curve for mid-morning mixing on Day 195 overstates the dilution at that particular time of the day. That's a time of day when the air parcel goes through the city where the emissions are occurring.

If you dropped it down a little bit on that day you would get greater concentrations around 10:00 a.m. or 11:00 a.m. You may in fact increase your O_3 prediction.

I think there are different reasons on different days.

JEFFRIES: Can you be specific about Day 159? I predicted it well with the older approach. Why is Day 159 so poorly predicted in this case, compared to the way it was before.

GIPSON: The trajectory changed significantly.

JEFFRIES: Where is the trajectory now?

GIPSON: It's still in the same general area.

JEFFRIES: It's further out?

GIPSON: It's moved, well, it's actually further up, too. So it shows the critical nature of getting the trajectory right.

WAYNE: I wonder if there is a possibility that in some of these cases with this characteristic curve, you're starting with such low mixing heights that some substantial amount of precursors is sequestered in the stratified air above the initial mixing layer, so that when you do your dilution you're ignoring a proportion of the contaminants that will eventually wind up in that parcel?

GIPSON: I'm sure. The model is simplistic in the sense that it does assume a uniform mixing under the mixing layer in the early morning.

WAYNE: And a lot of it above the mixing layer?

GIPSON: Yes. We did ignore precursors above the mixing layer. What we did here was vary the mixing height at sunrise, which is one of the inputs to the characteristic curve, and I varied that across the ranges of 100 m to 250 m.

That is what is showing up most of the sensitivity.

The emissions differences didn't really have that much of an effect.

However, we have no way of getting at how high the mixing layer is.

JEFFRIES: When you vary the mixing height like that, with that particular model, you're not only changing the dilution, the total dilution that's going to take place for the day, but you also change the mass of material that you start with.

WAYNE: Exactly.

JEFFRIES: There is a balance and it's clear that you can shift things dramatically by changing the ratio between how much material you start with and how much you're going to dilute it. So you can shift the distribution from initial conditions to emissions tremendously by changing that one initial mixing height up and down.

WAYNE: And the temperature structure doesn't necessarily show you what is immediately above that morning mixing layer.

JEFFRIES: The model, of course, doesn't take into account point sources that emit at elevations above the mixing layer. It is a simple model.

GIPSON: There are many more detailed approaches; it's a simplified approach.

DEMERJIAN: One suggestion you might want to consider is putting in layer averaging rates. My guess is it will raise those numbers.

JEFFRIES: Won't he have to carry layers in the vertical structure, then?

DEMERJIAN: No, what I'm saying is that he can use an integrated average for the mixing layer height.

JEFFRIES: Okay. The numbers will keep going up as the mixing --

KELLY: Did you say that the mixing is about 20%/h more than the standard EKMA? You said about 23%?

GIPSON: Standard is 3%/h under the old exponential. These mixing depths changed on the order of, starting, say, at 100 m in the morning at sunrise, up to 2000 m on some days in the afternoon.

JEFFRIES: Two hundred seventy-five with the nine hundred.

DEMERJIAN: It might be easier, just to draw it on the board, just the profiles.

JEFFRIES: The 3% is for the standard Dodge in Los Angeles with the 600 to 7, whatever. That is only 3%/h.

When you use the exponential shape in these, of course, it's the same overall dilution. You're still going from 100 to 900. You just get there differently. So it is the same total dilution on Day 275, for example, you may start at 100 --

KELLY: There's hardly any dilution at all at that height.

JEFFRIES: That's right, 3%/h. Here it could be 900%. But individual days may start out at 100% and go to 1900%.

GIPSON: I think that's the exponential shape that was originally used in the Los Angeles case. Of course, it's only 3%. That's a very small change. But that's almost, in effect, a straight line.

In fact, if you use the characteristic curve with the same limits, you get the same answer. The changes are small.

JEFFRIES: I will show you some individual mixing heights calculated by three or four different ways tomorrow.

DODGE: Are there any more questions?

MEYER: One of the points Mr. Gipson mentioned was that we had a lot of trouble using surface wind data to come up with reasonable trajectories that make the model work well.

One thought we had was it might be better since people are unlikely to have anything other than surface wind data to rely on pollutant concentration data to infer some kind of trajectory and then just use that.

In effect, that's like what's done in Level III. We assume the scenario based on the concentration data and simply use the wind data to establish that, at least, the site observing the peak O_3 is downwind from the city.

I would like to hear people's reactions to an approach like that. That is, not directly using wind data to produce trajectories, but instead, trying to draw inferences about an approximate trajectory based on the concentration information that we have.

WALKER: May I respond to that?

Some recent data put together on an episode that occurred just last month in Houston, TX, where wind data were plotted hourly during the episode, revealed some very interesting patterns.

The only explanation of the wind vectors that could be made was that the winds were blowing at each other and going up. The heat element affected rising air currents.

I think under these conditions, deciding what the true trajectory is is extremely difficult.

The synoptic trajectory at that time was quite different from any of the surface winds. The synoptic wind was from the northeast but the surface wind was from the southeast and the northwest for a good part of the day.

So during episode conditions where you had low winds, it was very hard to be sure what your trajectory was.

McKEE: I would like to ask a question about using ambient air concentrations to trace a trajectory. First of all, what contaminant did you use? Or contaminants?

MEYER: All we really did was look at the peak O_3 concentrations, let's say in the St. Louis area, and noted what time of day the concentrations occurred. Then we looked at the surface wind data and reassured ourselves that at least the wind wasn't blowing in the opposite direction so those peak O_3 concentrations weren't upwind from the city.

Then we assumed that the air parcel started in the center of the city and moved towards where the peak O_3 was observed.

JEFFRIES: It's assumed.

McKEE: Yes, that wouldn't work in Houston because, first of all, O_3 precursors do not originate in the center of the city to a major extent.

Secondly, the variation of O_3 with location within the city is quite great. We don't have enough monitoring stations to describe the O_3 isopleths accurately over the area of the city at any one particular time, but we have several reasons for believing that O_3 may change rather significantly if you move crosswind of the trajectory by as little as a mile or two.

We know from having stations 5 or 6 mi apart that one station may show O_3 at better than 0.2 ppm. A station crosswind from the prevailing air movement at that time and distant from the first station by as little as 5 mi may show O_3 in the natural background range of 0.04 or 0.05 ppm.

So, I don't think you could use O_3 concentrations to determine what the trajectory was unless you had a monitoring station on each square mile of a rectangular grid or some totally impossible number of stations like that.

MEYER: Well, again, I don't think we are talking about applying a fine-tuned trajectory or anything like that, just an approximation.

McKEE: Well, if you vary 4 to 1 or 5 to 1 over a distance of 5 mi, that's hardly fine tuning. That's a gross difference.

JEFFRIES: We have two airshed modelers here. I'd like to know how they go about getting to the problem.

The EKMA models specify the wind flow in every single grid. How do they do that? Same data? Not the same data? Some other method?

KILLUS: It is quite typical that airshed models have what seems to be quite a reasonable pollutant cloud that is somewhat misplaced, by as much as 60° off what was likely to be the correct trajectory.

In our first EKMA model, for example, we found that the trajectory was more west of the city, whereas the actual pollutant cloud, as drawn by observers looking only at the air quality monitoring data, was going more or less northeast of the city.

The same sort of thing happened out in St. Louis.

JEFFRIES: These are being derived from surface wind data?

KILLUS: These are being derived from surface wind data.

JEFFRIES: Five-layer model?

KILLUS: That's right, three, two, three, four.

So I would actually suggest that in a circumstance like you described in Houston, if one has the peak O_3 at a particular station outside the city, and knows and observes that 5 mi away from that one has very close to background values, far from being a circumstance where you are limiting the possibility of drawing your trajectory from the O_3 monitoring data, you have, in fact, described a very precise trajectory from the O_3 monitoring data.

You know that the O_3 precursors are being emitted at a fairly narrow source area and you know pretty much where the receptor site is.

If one then draws a line between the two, one would draw that trajectory. And in some cases we recommend it for airshed modeling.

If you see the O_3 pollutant cloud being convected 30° off because of errors in surface monitoring, you might very well just go in and rotate the wind fields and see how much better you can do this.

Trying to prepare a large wind field from extremely noisy and oftentimes biased wind data is at present one of the largest single errors in airshed modeling.

APPENDIX 4-1

SCATTER DIAGRAMS FOR LEVEL III MODEL PERFORMANCE IN ST. LOUIS AND PHILADELPHIA

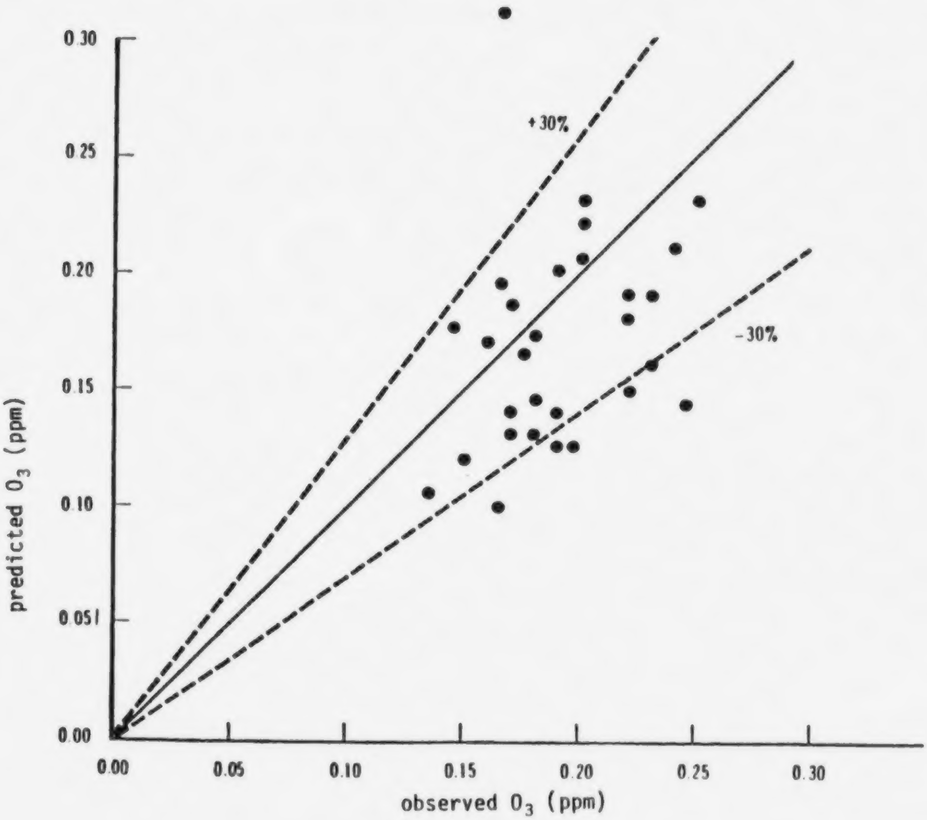

Figure 4A-1. Observed O_3 (ppm) for Philadelphia EKMA analysis 1982 SIP.

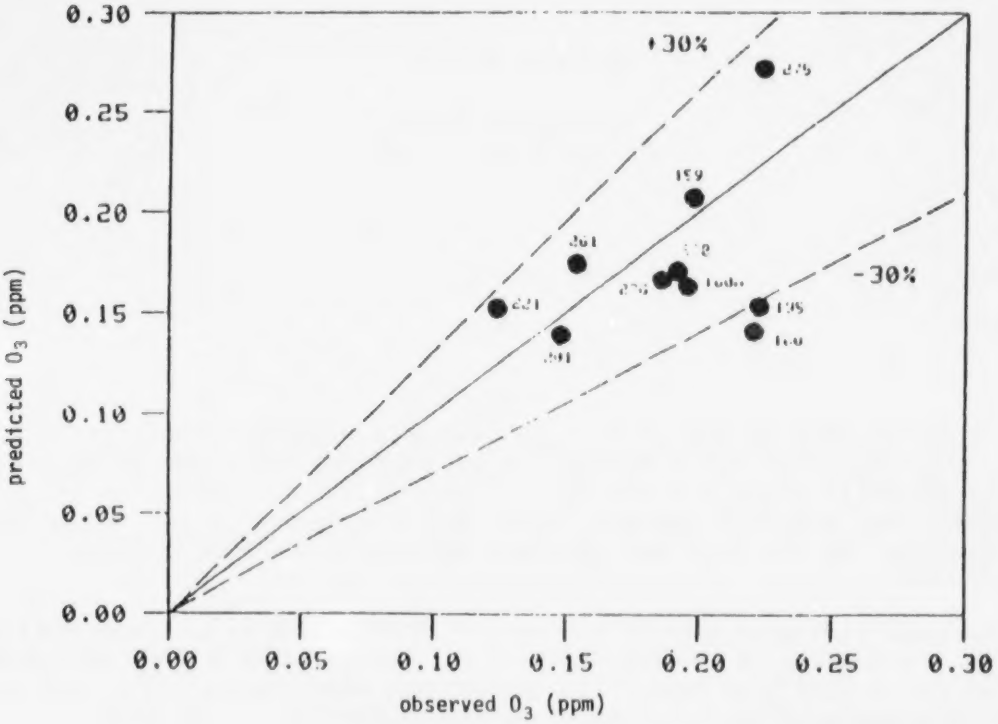

Figure 4A-2. Level III EKMA U.S. air quality (St. Louis RAPS).

5. APPLICATION OF EKMA TO THE HOUSTON AREA

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ABSTRACT

Ozone, nonmethane hydrocarbon, and oxides of nitrogen data gathered during the summers of 1977 and 1980 have been analyzed as a test of the EKMA predictive model. Data from six ozone monitoring sites, five oxides of nitrogen sites, and five nonmethane hydrocarbon sites were used. Predictions were possible for 114 days, and data were plotted on the standard-EKMA isopleth set.

Analysis indicated that 53 days should be discarded as an inappropriate test of EKMA because of adverse meteorology. The validity of EKMA was judged against the 61 remaining days. EKMA predictions were found valid (± 20%) for 20 days, underpredictive for 5 days, and overpredictive for 36 days.

Special attention was given to the "heatwave" period of June to July, 1980, which produced little ozone. Lack of adequate photochemical initiation was deemed to be the principle cause of overprediction. An attempt should be made to incorporate improved initiation factors into EKMA.

The prevailing nonmethane hydrocarbon:oxides of nitrogen ratio in Houston was found to be 11 to 1. Scenarios regarding the degree and method of abatement necessary to achieve the ozone standard are discussed. None are deemed feasible.

INTRODUCTION

The Houston Area Oxidant Study (HAOS) gathered a large amount of aerometric data in Houston during the summer of 1977. Included were ambient air data taken at numerous sites for ozone (O_3), nonmethane hydrocarbon (NMHC), and oxides of nitrogen (NO_x). SRI International in its analysis project completed for HAOS in 1979 carried out a preliminary Empirical Kinetic Modeling Approach (EKMA) correlation using these data (Ludwig and Martinez, 1979).

In SRI's work, peak O_3 values for 54 days in 1977 were predicted using standard-EKMA isopleths. Nonmethane hydrocarbon and NO_x values were obtained from monitors at five centrally located sites in Houston, TX. Predicted O_3 values were compared with the observed maximum O_3 values for the day. In SRI's methodology, only those days were evaluated for which values for both 6:00 a.m. to 9:00 a.m. NMHC and 6:00 a.m. to 9:00 a.m. NO_x were available from at least three central sites. Missing data severely restricted the number of days that could be studied and, in part, contributed to uncertainties in the final results. To study the value of EKMA as a predictive tool more decisively, the EKMA correlation was repeated using the same data from 1977, but supplemented with recent data available for June and July, 1980. As a result, 114 days were defined for which an EKMA prediction could be made.

METHODS

Hydrocarbon (HC) and NO_x monitors were centrally located (McGregor, Crawford, Clinton, Mae Drive, Parkhurst, and Aldine) and appear on the average to sense pollutant concentrations in the central city and West Ship Channel area. During this study, a large number of O_3 monitors were in operation. With most wind directions, one or more monitors were located downwind of the core complex. Thus, the availability of data and the location of the monitors would appear to conform to the concepts of the EKMA methodology, which attempts to relate 6:00 a.m. to 9:00 a.m. precursors in a core area to the subsequent O_3 maximum in a downwind direction (EPA, 1977).

For the purposes of this study, the robustness criteria was relaxed to 2-2; that is, two or more 6:00 a.m. to 9:00 a.m. NMHC values, plus two or more 6:00 a.m. to 9:00 a.m. NO_x values, were required in each average used for any EKMA prediction. SRI used a 3-3 robustness criteria that severely limited the number of days for which a prediction was possible. As a result of this change, plus the addition of the 1980 data, 114 days were found during May through September, 1977, plus June through July, 1980, for which a prediction could be made.

Predictions were made by plotting each day's average 6:00 a.m. to 9:00 a.m. NMHC and NO_x values on the standard-EKMA isopleth diagram and then reading back the predicted daily maximum O_3 concentration. The isopleth curves were interpolated as necessary (see Figure 5-1).

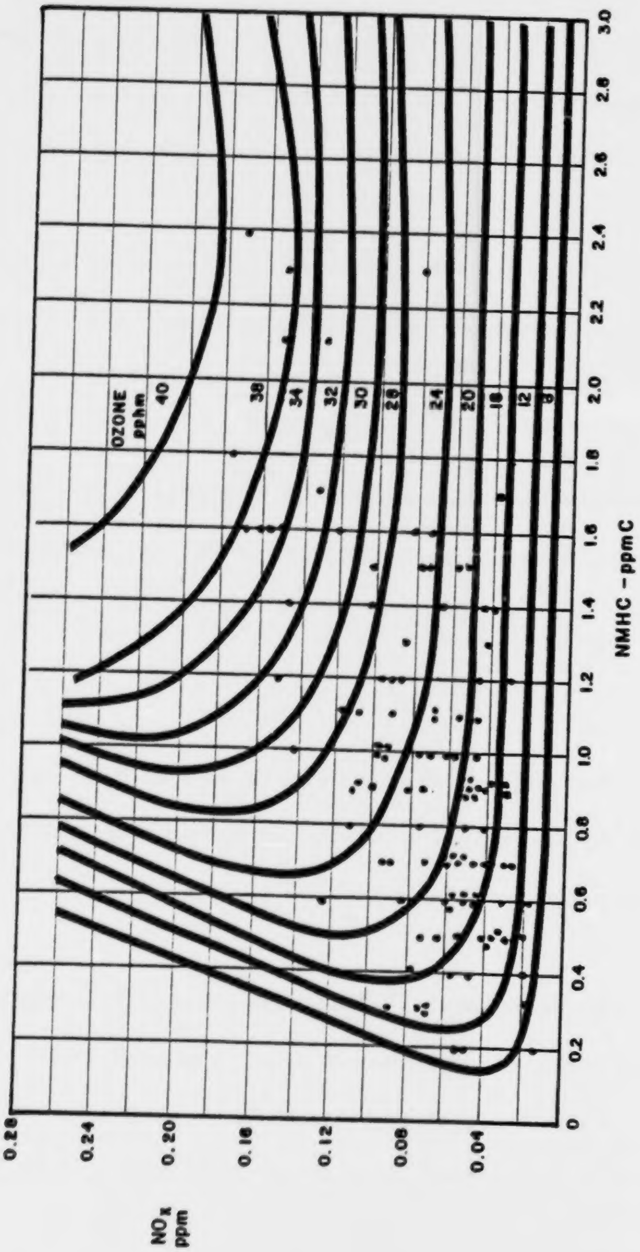

Figure 5-1. 114 predicted days on standard O_3 isopleth diagram.

When predictions were completed for all 114 days, many of them quite evidently had failed to test EKMA for factors that were obvious from the weather records. To investigate this matter further, meteorological data as follows were tabulated for each day: 6-h wind distance (9:00 a.m. to 3:00 p.m.), 6-h wind direction, 6-h sky cover, and noontime temperature.

All days were discarded if the 6-h wind vector exceeded 50 mi or if the 6-h sky cover exceeded 60%. Cloudy days or days with high wind produce little O_3, and thus cannot be regarded as testing the validity of EKMA.

The exact cut-off levels were fixed based on analysis of the actual data. Table 5-1 presents the pertinent data supporting the cut-off levels used. Interestingly, temperature proved not to be a key factor, and hence was not used.

Some data available for morning mixing heights appeared to be significant and would have been used as an exclusion criterion except that values were available only for a minor portion of the period (Table 5-2).

About half of all predicted days (53) were thus classified as E or explained failure days. Decisive days (non-E days) numbered 61 for this study (27 for the SRI study). Values for the 61 days are plotted on an EKMA diagram (Figure 5-2). All 114 days predicted are plotted in Figure 5-1.

TABLE 5-1. CHECKING PREDICTED DAYS WITH HIGH ADVERSE FACTORS

Date	6-h Wind Distance (mi)	6-h Sky Cover (%)
5/1	45	63
5/11	29	90
6/1	34	70
7/9	28	67
7/12	48	23
7/14	37*	60
7/26	32	60
6/27/80	48	0

*Rain

TABLE 5-2. O_3 VERSUS MIXING HEIGHT*†

Mixing Height	> 250 m	> 100 m	< 100 m
$O_3 > 0.2$	1	5	10
$O_3 > 0.1$	9	14	11
$O_3 < 0.1$	37	13	6

*Days = 5-9/1977.

†Total days with mixing height data = 106.

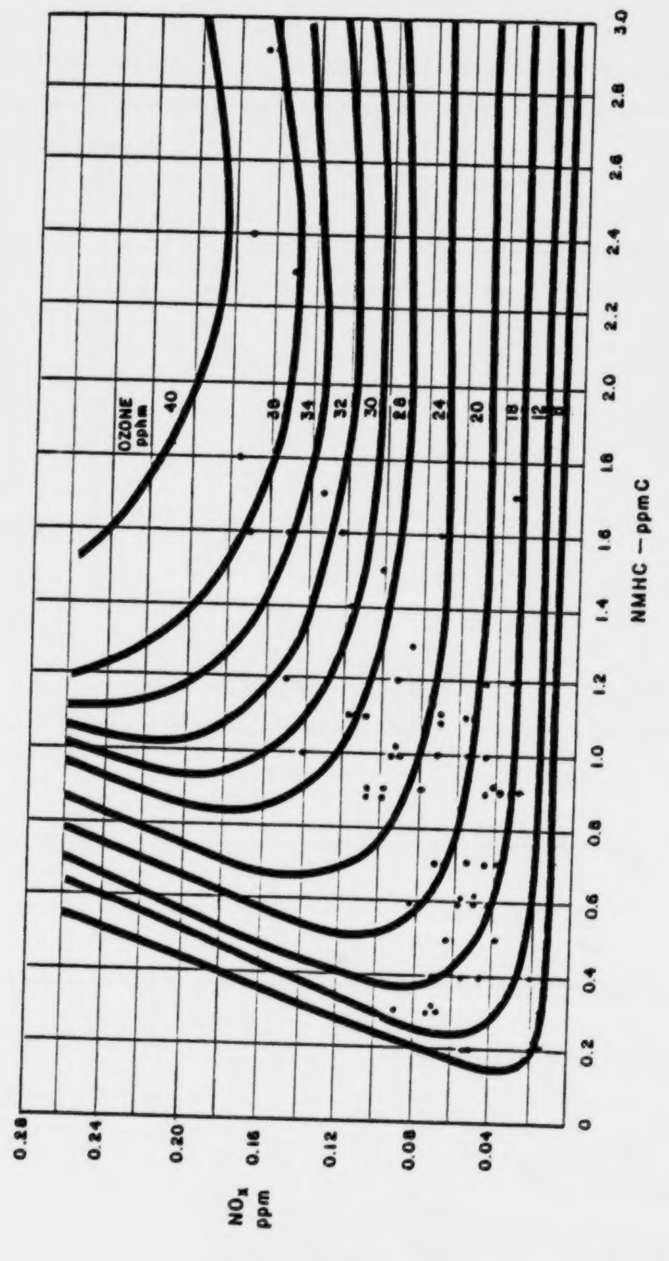

Figure 5-2. 61 decisive days on standard O_3 isopleth diagram.

RESULTS

Inspection of Figures 5-1 and 5-2 reveals little difference between them. However, this similarity was expected. The position of each point depends entirely on the precursor analytical results -- not on O_3 formation. There was never reason to expect that the E days, which were excluded from Figure 5-2, would belong to a different subgroup with respect to precursor concentrations.

The bulk of the points (days) lies in the region of the EKMA grid where the O_3 isopleths are very flat, suggesting that the formation of O_3 in Houston will be relatively insensitive to HC abatement. Real-world results have confirmed this suggestion; indeed, predicted O_3 levels, with the exception of a few cases, were critically dependent on the NO_x concentration, but were scarcely sensitive to NMHC concentration.

To judge better the validity of EKMA, a cross plot of measured maximum O_3 versus predicted O_3 was constructed (Figure 5-3). Only the 61 days from Figure 5-2 were used in plotting Figure 5-3.

The striking disclosure from Figure 5-3 is the random shotgun distribution of the decisive point group. The 45° line passes through the upper center of this pattern, but by no means its top. Broadly, EKMA underpredicted by more than 20% on 5 days (8% of 61), was within ± 20% of measured results on 20 days (33% of 61), and, for the remaining 36 days (59%

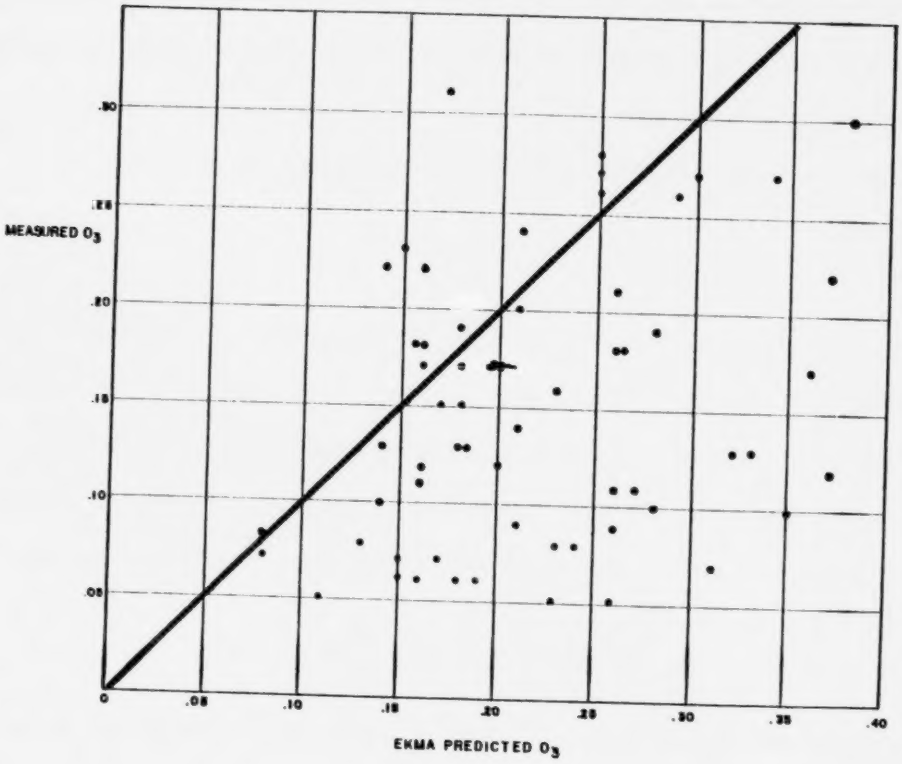

Figure 5-3. EKMA O_3 predictions versus actual observed O_3 values.

of 61), EKMA overpredicted actual O_3 by more than 20%. On 22 of the latter days, the predicted value was twice or more the actual value. In judging these results, note that all days for which the documented meteorology predicted a shortfall in photochemical O_3 production (E days) were eliminated from Figures 5-2 and 5-3.

This work does not support the contention that EKMA can supply an accurate upper-limit value for potential O_3. This conclusion is based on the 59% incidence of high (>20%) overprediction. This consistent tendency to overpredict is the most serious shortcoming of the procedure.

One may argue that the problem may be simply the lack of an O_3 monitor at the precise downwind plume position to find the true maximum. However, a real geographical miss is unlikely because the core area is very broad and so many analyzers were running during 1977.

In the course of this work, we noticed that the days that validated EKMA tended to occur in groups. These groups appeared to coincide with intense O_3 episodes. Since O_3 episodes are well known to be related to frontal passage, this possible association was investigated. In two of three cases where consecutive high O_3 days were noted, frontal passage was found to have occurred not more than 72 h prior. Thus, the theory that stratospheric O_3 injection can help initiate O_3 episodes received support. Apparently, initiation by stratospheric O_3 or by other factors is required to consistently induce O_3 production at the levels predicted by EKMA. This insight was a major finding of the study.

The June-July, 1980 period was included in this study partly because it was a noteworthy summer drought period for Houston. June and July established new records for the number of consecutive 100°F days in Houston. Little rain fell during the entire period. Winds were predominantly from the southwest, and generally lighter than those of the same period during 1977. This period of high temperatures, few clouds, little rain, and light winds was a conspicuously low O_3 period. On only 24 days was 0.1 ppm exceeded at any site ($3 > 0.2$). During the corresponding 1977 period, 0.1 ppm was exceeded on 34 days ($8 > 0.2$; $1 > 0.3$). Yet, pollutant concentrations were higher in 1980 (NMHC 0.84, NO_x 0.89) than in 1977 (NMHC 0.84, NO_x 0.65) (average of all robustness 2-2 or better days). Of all 2-2 robustness days, 18% verified EKMA in 1977, but only 14% in 1980. Apparently, the June-July, 1980 period represented a period of poor initiation. High temperatures, sunshine, and pollutant concentrations alone were not sufficient to guarantee a high O_3 period.

One additional insight was obtained from this study. The center of all points on Figure 5-1 is located at about NMHC = 0.9 ppm, NO_x = 0.08 ppm, corresponding to a HC:NO_x ratio of 11.25. Attainment of the 0.12 ppm O_3 standard by HC abatement would require a level of NMHC = 0.25 ppm or a 72% reduction (little changed from predictions made in 1973). Abatement by NO_x reduction to the same level would require NO_x = 0.02 ppm or a 75% reduction.

These figures are based on averaged 6:00 a.m. to 9:00 a.m. average values, not on peak values. Should peak values be used, the abatement level for HC's increases to 77.5% and for NO_x to 87.5%. None of these abatement scenarios is technically or politically possible.

DISCUSSION

EKMA appears to yield a scattered pattern of predictions that broadly overlap the range of actual O_3 values. Thus, some checking values will be found in every group predicted. However, many overpredicted values and a few underpredicted values will also be obtained. Yet, no other simple prediction scheme for O_3 can do any better, and most do worse.

It is the author's opinion that if the meteorological options available in the city-specific version of EKMA were carefully utilized the results would be improved. The initiation factor appears very desireable. Such a factor would endeavor to quantify everything that bears upon the input of free-radical initiators to the photochemical process. Background O_3, stratospheric O_3, and day-to-day atmospheric recirculation would all be components.

EKMA does not appear presently to weigh input O_3 sufficiently heavily in the initiation process. Other models that are more cognizant of the initiation potential of input O_3 and other free-radical sources seem to be more successful in making specific day predictions and in coping with multiday episodes. However, these models are far more complex and expensive to use. The practicality of adding such a factor to EKMA without making the computation much more complex and at the same time creating a need for additional sophisticated input analytical information is questionable. However, it should be given some thought as the simplicity and convenience of the EKMA procedure justifies major effort toward its improvement.

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WORKSHOP COMMENTARY

JEFFRIES: Could we go back to the slide for decisive days on your isopleth diagram?

WALKER: Yes. That one?

JEFFRIES: Yes.

May I suggest that you multiply all the O_3 isopleth numbers by about a half and count the number of points above each one to see if the frequency distribution predicted by your points agrees with the observed frequency distribution.

WALKER: It would probably help, yes.

JEFFRIES: In effect, that's the method that I describe. You can count the number of points in each interval and do the proportion against what was actually observed. Then you can compare the frequency distributions instead of trying to do an absolute prediction of HC, NO_x, and O_3, on the same day, with the diagram.

It is very close. You could probably sit down and do it by hand very quickly.

WALKER: Yes, that distribution is not greatly different from the one you showed for St. Louis, really.

MARTINEZ: I am struck that it was so widely underpredicted. Pointing to the data, it is pretty clear to me that the HC's were way underestimated. If you had higher HC on that day you would have, of course, moved things over closer to the 45° line.

WALKER: Yes. I didn't attempt to critique the HC's. I just took what we had. That could well be. I wouldn't question that.

The HC and NO_x data are problematic. I think there were poor recovery data in many of the analyzers, which was disappointing. As you say, they are hard analyzers to run, but get really good results.

You can always worry about the quality of the data.

KELLY: Maybe this is a good time to say that when we did the bag radiations in Houston in 1977, we did get good agreement between predicted O_3 in the bags, using EKMA, and the observed O_3 in the bags, using Houston air.

You don't really need initiation under those conditions. I really question whether you need stratospheric O_3 to initiate photochemical O_3 formation.

WALKER: I recognize that a lot of people question this thesis, but I say that the bags are always contaminated with free radicals so they don't really constitute a test, whether the supply of free radicals is adequate or not.

KELLY: Whether they are contaminated with free radicals or not, you can look at the production of O_3 in bags at low amounts of precursors and see what the contamination is.

You can look for that with NO_x or HC. We don't find that there is an excess OH radical in those conditions.

WALKER: What you're saying is, it works in the bags, is that right?

KELLY: Yes. In other words, the OH that we would predict in the bags based on ethylene or NO_x loss experiments is comparable to what people measure in the air using spectrometers, or predict in the air, using models, for the OH radical. There wasn't any evidence for any excess OH radical.

What I think is happening is that these things occur together. These stratospheric intrusions in our data, which are traces of stratospheric air, bear that out. The berylium-7 problem is higher on the back side of a high pressure system. Stagnation and photochemical formation of O_3 are also higher on the back side of high pressure systems.

I'm not saying you're wrong. I'm saying that under conditions where there is a higher stratospheric input, you don't measure more O_3 downwind. I just don't think the cause is that initial stratospheric O_3.

I think the O_3 downwind of cities is the result of photochemistry.

WALKER: Yes, it certainly is. The question is, something to start the process, not that it adds to the process as much as you find downwind.

6. A COMPARISON OF THE EMPIRICAL KINETIC MODELING APPROACH MODELS WITH AIR QUALITY SIMULATION MODELS

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ABSTRACT

One method for testing a simple model such as the Empirical Kinetic Modeling Approach (EKMA) is to compare its performance with that of more complex models using the same input data. The many differences between EKMA and a model such as a complex grid model can be used to define a series of progressively more complex models. The steps in this model series can then be used to highlight significant factors that define EKMA.

The results of this study show that in the absence of wind shear, the simplistic dispersion treatment used in the EKMA model typically produces results that are very similar to those of models with more complete treatments of dispersion. However, differences in the chemical mechanism, dependence on hydrocarbon:oxides of nitrogen ratios, entrainment of reactive precursors, and other factors were all found to often lead to significant differences between the present Level III EKMA and more complex models. The study also found that the assumption of a linear relationship between emissions and the initial hydrocarbon and oxides of nitrogen concentrations does not always hold, especially in the presence of significant background hydrocarbon levels.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has defined three levels of modeling for use in 1982 State Implementation Plans (SIP's). Level III consists of a city-specific Empirical Kinetic Modeling Approach (EKMA) model used in accordance with a guideline document issued in March 1981 (EPA, 1981). Level II refers to more complex versions of EKMA, and Level I refers to large, sophisticated Air Quality Simulation Models (AQSM's) such as the SAI Urban Airshed Model.

In a recent study, we tested EKMA against more sophisticated modeling approaches using a series of intermediate models that fall between standard Level III EKMA and large-grid models such as the SAI Urban Airshed Model. The purpose of our study was not to demonstrate that EKMA models generate different results from other models or to determine whether such discrepancies are significant. In general, one can expect different models to generate different results. Instead, we wanted to find the main reasons for any differences in results that stem from the specific parts defining each of the models. To that end, we used the same input data to compare any two models, and the intermediate models we created were designed to test a minimum number of model differences between any two models.

The main points we wish to make in this presentation are as follows:

- EKMA has two parts (a trajectory model and a diagram).

- The EKMA trajectory model treats chemistry more accurately than many other models, but treats dispersion simplistically.
- Neither its accurate chemical treatment nor its simplistic dispersion treatment has been shown critical to the reasonable use of the model, except in cases involving wind-shear effects.
- The results of most comparisons involving the use of the diagram are reasonably close except in the definition of hydrocarbon: oxides of nitrogen ($HC:NO_x$) ratios and in situations where background is important.
- Initial concentrations and $HC:NO_x$ ratios do not respond linearly to controls, especially when background is important.

METHODS

We first need to clarify our own generic use of the acronym EKMA. For our purposes, EKMA is an approach to estimating the changes in maximum ozone (O_3) expected in some urban area resulting from changes in emissions. This approach implies the use of an O_3 isopleth diagram defined by an ordinate and abscissa that can be related to NO_x and HC precursors. Each point on the diagram can be associated with the simulated 1-h O_3 maximum generated by the execution of a computer-coded trajectory model, using the inputs specified by the ordinate and abscissa values associated with that point on the diagram. Our definition of an EKMA trajectory model includes any moving-column model that treats at least the chemistry within that column, along with some treatment of dispersion. This generic definition allows us to construct highly complex versions of EKMA without needing to create names for each new version.

To a large extent, we have been working on the next generation of EKMA models by testing the effect of added degrees of sophistication to the existing Level III EKMA model. The models we have constructed might be called Level II EKMA models, but we have not been using these models independently for control-strategy purposes. In general, we have used these models with the same data base as that of some highly sophisticated or Level I models. However, we have delivered one of these Level II models to the South Coast Air Quality Management District (SCAQMD), and they will be using this model as part of their 1982 SIP.

GRID MODEL COMPARED WITH LEVEL III EKMA MODEL

Most of the work reported here was funded under EPA contract. Table 6-1 presents the most recent results obtained under this contract for Tulsa, OK. The table compares the standard Level III EKMA model, the same model with the Carbon Bond II chemical mechanism (CBM), and the SAI Urban Airshed Model. In this particular comparison, the EKMA models were applied according to the 1982 SIP guidelines except that the design O_3 values were chosen to be equal to the value predicted at the Apache monitoring site by the SAI grid model.

Several reasons exist for presenting these particular data here. The results shown supersede those published in our final report to EPA covering the Tulsa study (Whitten and Hogo, 1981). This update represents a cycle we consider very important to the modeling process. The original EKMA study

TABLE 6-1. LEVEL III EKMA RELATIVE TO SAI AIRSHED MODEL*

Control				
HC (%)	NO_x (%)	Airshed Model (ppm O_3)	EKMA Model (ppm O_3)	EKMA/CBM† Model (ppm O_3)
(base case)		0.127	(design)	(design)
32	7	0.104	0.115	0.95
49	8	0.096	0.10	0.075
75	7	0.087	0.07	0.04
18	-2	0.117	0.123	0.11

*Apache station, 29 July 1977; observed O_3 = 0.133.
†Carbon Bond II mechanism.

helped identify the importance of high HC concentrations used aloft in the early grid-model simulations. Subsequent grid-model simulations employed much lower HC concentrations aloft and adopted several other modifications. Thus the simultaneous use of a simple model such as the Level III EKMA trajectory model along with a more complicated one can help identify areas of the modeling exercise that significantly affect the results of the complicated model and may require reconsideration.

Table 6-1 demonstrates the point made earlier, that is, different models merely generate different results, providing little insight into why the results may differ. The results from the modified model (i.e., the same model using the Carbon Bond II chemical mechanism) demonstrate that matching the chemistry of the EKMA trajectory model and the grid model creates a model that is much more sensitive to HC control than either of the original models. Hence, any attempt to create an "improved" EKMA model by updating only the chemistry may generate EKMA results that are farther away from those of the more sophisticated models. The standard Level III EKMA model apparently has several compensating discrepancies when compared with more detailed models such as this grid model. However, we know of no guarantee that the discrepancies will consistently compensate for each other.

GRID MODEL COMPARED WITH LEVEL II EKMA MODEL

Table 6-2 presents the latest results for Tulsa obtained using the trajectory model developed in our studies for Level II EKMA. Whereas we obtained the results shown in Table 6-1 using the relative isopleth methodology of EKMA, we did not need this methodology to obtain the results shown in Table 6-2 because the absolute predictions were fortuitously identical. We use the term fortuitous because the many remaining discrepancies between the models have apparently compensated for one another. Again, there is no guarantee that the compensations will remain, but considerable effort has been expended to ensure that the remaining discrepancies between these models are consistently small.

Several discrepancies between these models are worth noting. The grid model uses steady-state approximations and the Crank-Nicholson integration scheme to integrate the ordinary differential equations generated by the

TABLE 6-2. LEVEL II EKMA RELATIVE TO SAI AIRSHED MODEL*

Control HC (%)	Control NO_x (%)	Airshed Model (ppm O_3)	Level II EKMA Model (ppm O_3)
(base case)		0.156	0.156
32	7	0.114	0.122
49	8	0.101	0.100
75	7	0.088	0.073
18	-2	0.138	0.132

*Region-simulated maximum, 29 July 1977; station-observed O_3 = 0.133.

chemistry, whereas the Level II EKMA model uses the Gear method with no steady-state approximations. In addition, the grid model follows four cells in the vertical direction, two within the mixed layer and two above. Mixing between cells, both vertically and horizontally, is governed by wind speed, temperature, stability, and surface roughness, all of which vary in space and time. The Level II trajectory model follows only one cell in the mixed layer; the concentrations aloft cannot be varied in time and must be specified as input. Both models, of course, assume instant mixing within one cell.

The grid model treats surface sinks for each species, and these surface sinks vary spatially. The grid model also treats eddy diffusion between the four cells. The trajectory model ignores both surface sinks and eddy diffusion. Further, whereas the grid model treats horizontal dispersion, the trajectory model ignores it.

Finally, emissions in the grid model can be added into each of the four cells plus the surface below the first cell; the reactivity of these emissions can vary in space, level, and time. The reactivity of the emissions added into the single cell of the trajectory model cannot be varied.

Note that the Level II EKMA model uses the data files prepared for the grid model, and the grid model identifies the time and place of the maximum O_3 concentration in a region. Thus, Table 6-2 is not intended as evidence that our Level II EKMA model can be used as a replacement for the grid model. In fact, our Level II EKMA methodology presumes the existence of a validated grid-model simulation prior to the trajectory simulations. Inputs for the Level II EKMA trajectory model are obtained from the grid-model files by using a special trajectory model similar to the SAI Urban Airshed Model. This special model can be operated backward in time using the surface winds from any point in space and time defined by the grid-model region. When operated forward in time, this model generates averaged information, such as hourly emissions, which can be used directly in the Level II EKMA trajectory model.

At this point it seems appropriate to explain the differences between our Level II EKMA model and the Level III EKMA trajectory model. Our model appears to provide results similar to the SAI Urban Airshed Model, when using the same data files and when wind-shear effects are not important. The differences between the Level II and Level III models are summarized in the following discussion.

The chemistry in the Level II model is the same Carbon Bond II mechanism currently encoded into the SAI Urban Airshed Model. An explicit propylene/butane mechanism is used in the Level III EKMA model. The starting time and length of simulation are optional in the Level II model. The maximum single-simulation time is currently 24 h, and multiple simulations can be linked. The Level III model starts at 8:00 a.m. and lasts only 10 h.

Mixing heights are input hourly and internally interpolated linearly in the Level II version, in contrast to the input morning and afternoon heights, with interpolation based on a special characteristic curve, used in the Level III model. Reactivity data can be input using different splits for emissions and initial conditions, background and aloft, in the Level II model. In the Level III model, the initial concentration reactivity and emission reactivity must be identical; transported surface and aloft reactivity is fixed at 10% propylene, 90% butane, and zero aldehydes.

In addition to the regular HC species and O_3, the Level II model provides for entrainment of peroxyacetylnitrate (PAN) and the intermediate carbon-bond species GLY or BZA. These species have been found to act as important reservoirs of reactivity.

Finally, the temperature can be input hourly and interpolated linearly in the Level II model, but is fixed in the Level III model. Only the Level II model can treat the emissions and chemistry of carbon monoxide (CO).

We found all of the differences between the Level II and Level III models to be important under some circumstances, but found none of the differences between the grid model and the Level II model important under most of the circumstances studied. The most important difference between the Level II and Level III model tended to be the chemistry; however, we found that most of the difference could be explained by the ratio of rate constants between peroxy radical-nitric oxide (RO_2 + NO) reactions and the hydroxyl-nitrogen dioxide (OH + NO_2) reaction. Updating that ratio in the standard Level III chemistry to the value of 0.86, the ratio value used in the grid-model chemistry, typically increased the peak O_3 simulated in the Level III EKMA model by 30%.

Gross differences appear between the information provided by a grid model and a single-moving-cell model such as the Level II model. The grid model simulates the entire pollutant field, whereas a trajectory model simulates only a single Lagrangian air parcel. However, the grid model encompasses the Level II model, and the results between models can be compared at that point. The most significant differences in results between the single cell and an equivalent spot in the grid model seemed to occur when wind shear was important. Other differences in results can, for the most part, be explained by spatial variances in reactivity, surface sinks, and aloft concentrations.

We have attributed large relative, but small absolute, differences to the integration schemes used during nighttime simulations.

ELIMINATION OF AMBIENT HC:NO_x RATIOS

The use of the isopleth diagram in the Level III EKMA model requires obtaining ambient HC:NO_x ratios and a design O_3 value. The results shown in Table 6-1, for instance, were obtained using the HC:NO_x ratio of 9.1, which was computed according to the EPA guidelines for use of the Level III EKMA model. Our research and experience have led to a growing concern regarding this aspect of EKMA. Hence we propose an alternate, and hopefully improved, method of using the isopleth phase of EKMA. The new method essentially substitutes an emissions inventory for the ambient HC:NO_x ratio and starts the simulation early enough so that the overall simulation is dominated as much as possible by emissions rather than by the initial conditions.

Several concerns regarding the present use of ambient HC:NO_x ratios must be addressed before discussing this method, however. Wide fluctuations are often seen in ambient measurements and averaging measurements from nonepisode days to reduce the statistical noise may not be appropriate for use on episode days. Although some of the fluctuations may currently be the result of poor quality instrumentation and techniques, the use of accurate and robust measurements may still produce large fluctuations. Many fluctuations are caused by micrometeorological effects stemming from local emissions and by poor mixing, which can occur during the morning hours. In some cities such as

San Francisco, the episode trajectories may not be in the urban core at 8:00 a.m. when the HC and NO_x data are obtained. Such data would clearly be inappropriate.

A basic premise of EKMA requires that the initial conditions specified by the axis of the isopleth diagram should be linearly related to the emissions of precursors. When compared to more sophisticated models, this premise can be proven false, and the degree of failure can be shown to be a function of background HC's.

A measure of the trajectory model's accuracy in simulating the design O_3 value for the episode conditions used is difficult to obtain. The fluctuations and uncertain appropriateness of the measured HC and NO_x data obscure this type of validation.

An emission-oriented approach has been developed for constructing and using isopleth diagrams. This new approach eliminates these concerns and appears to have several additional advantages over the old isopleth diagrams.

First, although emissions inventories may currently have many errors, the most recent series of corrections and reestablishments seems to show only small overall changes in reactivity and total integrated amounts of emissions. Therefore, fluctuations in ambient measurements are small.

Another advantage of the emission-oriented approach is that whereas the quality of emissions inventories can improve, the micrometeorological effects that can influence HC:NO_x ratio data cannot. Thus, the emission-oriented approach offers the opportunity for refinement. In addition, emissions on episode days do not usually differ significantly from emissions on nonepisode days, so the averaging of emissions information appears to be more appropriate than the averaging of HC:NO_x ratios.

When the initial conditions of the model are not important, a starting time earlier than 8:00 a.m. need not have accurate mixing height inputs until 8:00 a.m. because the chemistry of fresh emissions is not signficantly affected by concentration until the sunlight intensity has increased. Also, the definition of a trajectory path before 8:00 a.m. is not critical unless the emissions inventory is gridded and extreme fluctuations are found between alternate grid squares. Presumably, the trajetory path on episode days would be expected to pass over major emissions before 8:00 a.m..

An additional advantage of the emission-oriented approach is that linearity between the emissions and the axis of the isopleth diagram is automatically and directly built into the model.

The 1,1 point on the new-type diagram in Figure 6-1 represents the O_3 generated by the trajectory model using the base-case emissions inventory and model conditions. This point provides an instant and obvious indication of

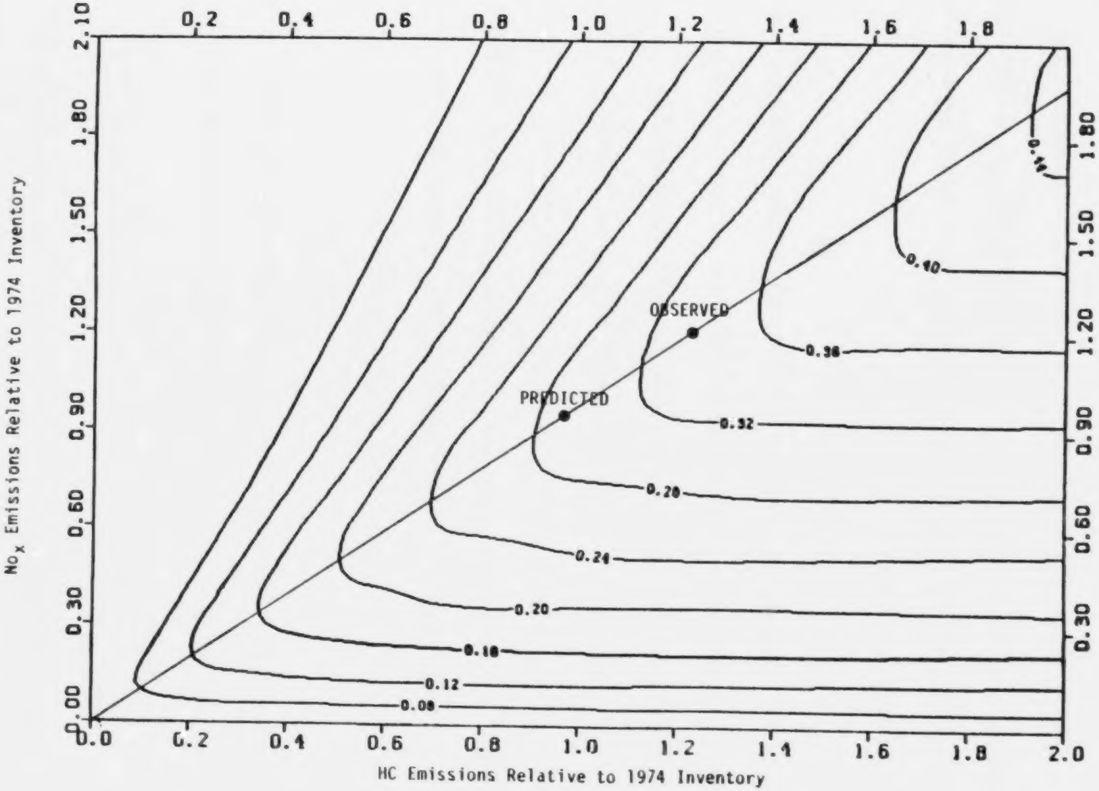


Figure 6-1. Emission-oriented Level II EKMA isopleth diagram based on a 26 June 1974 trajectory in Los Angeles.

model validation when this base-case O_3 value is compared to the design or observed O_3 value.

The diagonal line through the 1,1 point from the origin takes the place of the $HC:NO_x$ ratio line used in the standard EKMA model. The distance along this line between the design O_3 and the 1,1 point represents the combined discrepancy between the model and the observations. Two major types of discrepancies are the overall dilution and the overall emissions total. Both of these are assumed to be linear when moving up or down this diagonal line.

First let us explore in detail some of the problems associated with the use of $HC:NO_x$ data. For Tulsa, the $HC:NO_x$ ratio varied beween 380 and 0.9 for the period from July through September at the six monitoring stations. The minimum single-station variation (recorded at the Tulsa County Health Department) ranged between a maximum of 31 and a minimum of 1.7 during this period. The minimum standard deviation also occurred at the same station; this minimum standard deviation value was 5.7 about a mean ratio of 8.7. Hence the fluctuations in data can be large. The use of some range of values for the ratio to bracket the situation eliminates part of the advantage EKMA might have over previous approaches to control-strategy estimates.

Table 6-3 demonstrates our test of the premise concerning the linear connection between the 8:00 a.m. concentrations and changes in emissions. The table presents two comparisons for a Level II trajectory started 22 h earlier, for which the simulated air originated over the Pacific Ocean and moved inland

TABLE 6-3. CONCENTRATION AT 8:00 A.M. AFTER 22 H OF MODIFIED EKMA SIMULATIONS

Low Background (0.03 ppm RHC)

Species	1974 Base Concentrations (ppm)	Controlled-Emissions Concentrations (ppm)	Percentage Change (55 HC and 38 NO_x)
Paraffinic HC	0.74	0.35	53
Carbonyls	0.068	0.029	57
NO	0.025	0.021	16
NO_2	0.067	0.037	45
NO_x	0.092	0.058	37

High Background (0.18 ppm RHC)

Species	1974 Base Concentrations (ppm)	Controlled-Emissions Concentrations (ppm)	Percentage Change (55 HC and 38 NO_x)
Paraffinic HC	0.95	0.46	52
Carbonyls	0.12	0.073	39
NO	0.006	0.0015	75
NO_2	0.057	0.0116	81
NO_x	0.063	0.0131	79

over Los Angeles. The simulated air cell arrived at the coast at approximately 2:00 p.m. on the previous day, and remained under the influence of the emissions inventory from then on. Note that when a low background of approximately 0.03 ppmC HC's was assumed, the 55% control of the HC emissions resulted in a near-linear reduction of the paraffinic HC concentration in the model at 8:00 a.m. on the second day of the simulation. The carbonyl concentration was similarly reduced; paraffinic carbon was reduced 53% and carbonyls 57% from the 55% control of emissions. Oxides of nitrogen were also fairly linear, with a 35% reduction from a 38% control. However, the response of NO and NO_2 was not consistent; the $NO_2:NO_x$ ratio changed from 0.73 to 0.64 with control.

When a background of 0.18 ppmC HC was assumed, the response of the model was not as linear with regard to emissions. The 55% reduction in HC emissions produced a 52% drop in paraffinic carbon, but only a 39% reduction in carbonyls. Since the latter are highly reactive, the overall reactivity of the 8:00 a.m. mix actually increased. The 38% NO_x control that accompanied the HC control resulted in a 79% reduction in overall NO_x, but the $NO_2:NO_x$ ratio showed very little change for this high background case. Note that the controls should have reduced the 8:00 a.m. $HC:NO_x$ ratio, if linearity were true; but, according to the model used for this test, the 8:00 a.m. $HC:NO_x$ ratio actually increased significantly. The reason for this anomaly stems from the high HC's assumed for the background air. Hydrocarbons oxidize to intermediate compounds, which in turn photolyze to radicals that convert the NO_x to nitrates. Hence, the linearity premise breaks down as background HC's increase in concentration; the initial $HC:NO_x$ ratio may not even respond in the same direction as expected from the emissions controls.

Another element of concern for the HC:NO_x ratio is the appropriateness of urban core data for all episode simulations. According to our analysis of the grid-model files used for the 1979 SIP in San Francisco, the episode trajectory was out over the Pacific Ocean at 8:00 a.m.; the grid model used in this case was the Lawrence Laboratory Livermore Regional Air Quality (LIRAQ) model. Using the LIRAQ model wind fields and emissions inventory, we obtained reasonable agreement between the Level III EKMA model and the LIRAQ model. Table 6-4 demonstrates that this trajectory was completely dominated by the emissions after 8:00 a.m.. Post-8:00 a.m. emissions are normally input to the EKMA model as a function of the initial conditions, so the emissions inputs for the simulation results shown in Table 6-4 were each changed to generate the same concentration contribution from emissions within the model. Hence, Hence, Table 6-4 actually shows total lack of sensitivity to initial conditions for this trajectory.

TABLE 6-4. VALUES FOR MAXIMUM O_3 VERSUS VALUES FOR INITIAL CONDITIONS*

NO_x (ppm)	HC (ppmC)	Maximum O_3
0.003	0.03	0.197
0.003	0.01	0.196
0.003	0.003	0.194
0.001	0.03	0.198
0.001	0.01	0.196
0.001	0.003	0.195
0.0003	0.03	0.197
0.0003	0.01	0.195
0.0003	0.003	0.195

*26 July 1973 trajectory No. 1.

An attempt to use EKMA as part of the 1979 SIP had to be abandoned because the HC:NO_x ratios measured in the urban core were so low that no O_3 lines intersected the HC:NO_x lines. Our application of EKMA, therefore, shows that the standard city-specific version of EKMA could have been used; however, the HC:NO_x data were inappropriate. We also generated the isopleth diagram(s) that might have been used in the 1979 SIP. Since the trajectory model used to generate the points on the diagram was not sensitive to the initial conditions, a new definition for the HC:NO_x ratio appropriate for applying EKMA was needed. An appropriate ratio was chosen to be whatever initial ratio was used to compute the emissions input for the trajectory model, so that the base-case simulation generated the proper concentrations dictated by the emissions density and mixing heights found in the LIRAQ files. Figures 6-2 and 6-3 present isopleth diagrams generated from two of the cases given in Table 6-4 for various initial conditions. Note that both isopleth diagrams are virtually identical even though the "design" HC:NO_x ratios to be used are 1 and 100, respectively. Table 6-5 presents the comparison of several LIRAQ and EKMA control-strategy predictions.

In conclusion, we wish to point out that the close agreement we were able to obtain among various EKMA models and other AQSM's stems from analysis of the precursor concentrations as a function of time. As long as the precursor levels are close, and the same chemical mechanism is used, one can reasonably expect similar O_3 levels to be generated in the models. Figure 6-4 presents typical results for the models we have studied. To emphasize our concern for more accurate estimates of background HC's, we conclude with one last

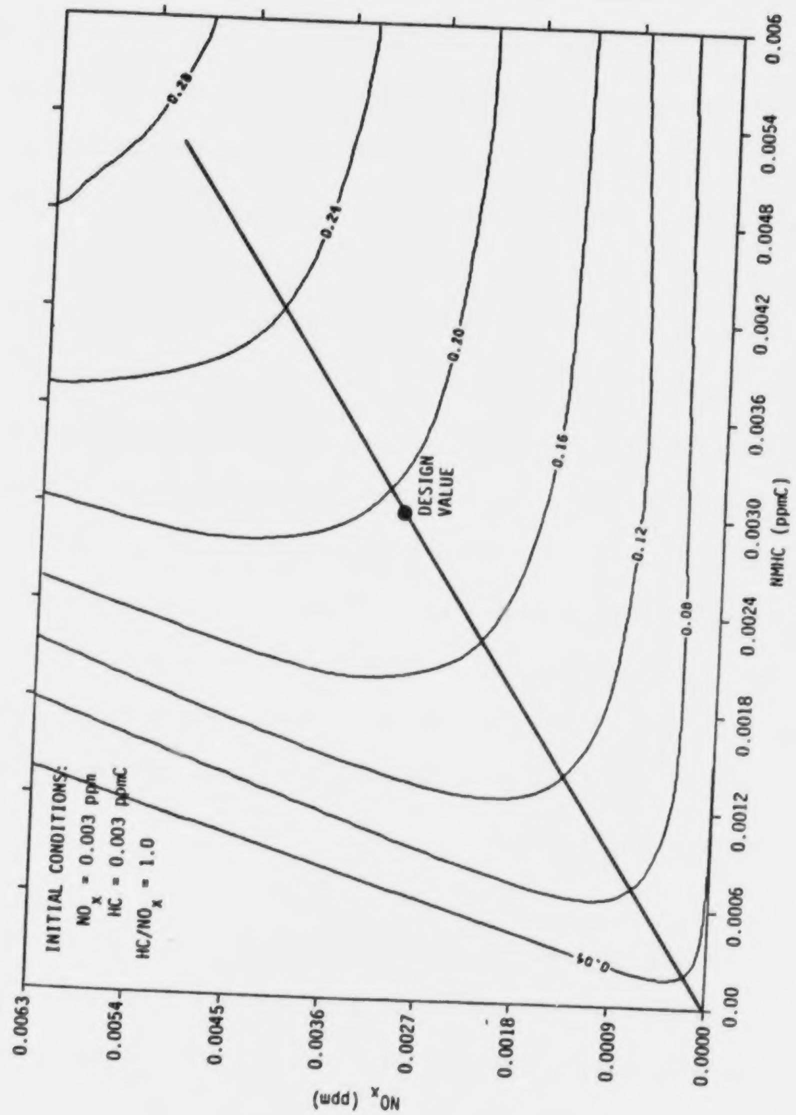


Figure 6-2. Isopleth for 26 July 1973: Trajectory 1--HC:NO_x ratio = 100:1.

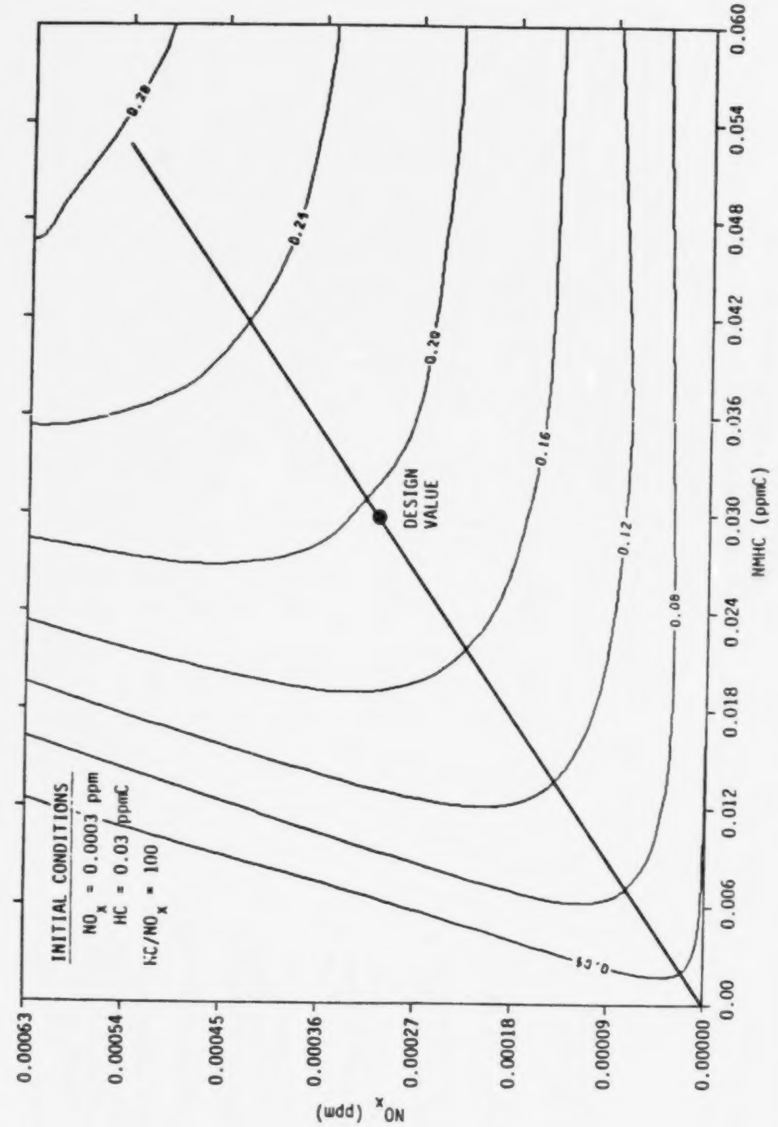


Figure 6-3. Isopleth for 26 July 1973: Trajectory 1--HC:NO_x ratio = 100:1.

TABLE 6-5. CONTROL-STRATEGY COMPARISONS FOR SAN FRANCISCO BETWEEN THE LIRAQ, EKMA/CBM, CITY-SPECIFIC EKMA, AND LEVEL III EKMA MODELS

Models Studied	Reduction %	HC:NO$_x$ Ratio Values							
	HC	0	20	40	60	80	40	80	0
	NO$_x$	0	0	0	0	0	20	40	40
LIRAQ worst-case 1985 emissions for 7/26/73		0.189	0.140	0.082	0.069	0.055	0.119	0.064	0.233
City-specific using Ozone Isopleth Plotting Package (OZIPP) (based on 0.189 maximum) 1975 emissions of 7/26/73		0.189	0.161	0.145	0.102	0.036	0.141	0.062	0.160
City-specific using OZIPP (based on 0.189 maximum) 1975 emissions for 7/24/74		0.189	0.162	0.127	0.070	< 0.02	0.135	0.048	0.172
City-specific using OZIPP (based on 0.189 maximum) 1975 emissions for 8/20/73		0.189	0.168	0.128	0.082	0.043	0.132	0.058	0.185
Average for three OZIPP runs		0.189	0.164	0.133	0.085	0.03	0.136	0.056	0.172
City-specific using OZIPP (based on 0.189 maximum) 1975 emissions for 7/26/73; HC:NO$_x$ = 1.0		0.189	0.169	0.142	0.098	0.036	0.143	0.060	0.160

(continued)

TABLE 6-5. (continued)

Models Studied	Reduction %	HC:NO_x Ratio Values							
	HC	0	20	40	60	80	40	80	0
	NO_x	0	0	0	0	0	20	40	40
City-specific using OZIPP (based on 0.189 maximum) 1975 emissions for 7/26/73; HC:NO_x = 100		0.189	0.165	0.146	0.105	0.040	0.145	0.063	0.160
City-specific using OZIPP (based on 0.189 maximum) 1975 emissions for 7/26/73; new-style isopleth		0.189	0.165	0.125	0.073	> 0.02	0.132	0.063	0.163
EKMA/CBM (based on 0.189 maximum) 1975 emissions for 7/26/73		0.189	0.161	0.122	0.078	0.038	0.134	0.053	0.172
Level III EKMA (based on 0.189 maximum 1975 emissions for 7/26/73		0.189	0.130	0.080	< 0.080	< 0.080	0.10	0.80	0.247
Level III EKMA using CBM (based on 0.189 maximum) 1975 emissions for 7/26/73		0.189	0.112	< 0.08	< 0.08	< 0.08	0.08	< 0.08	0.313

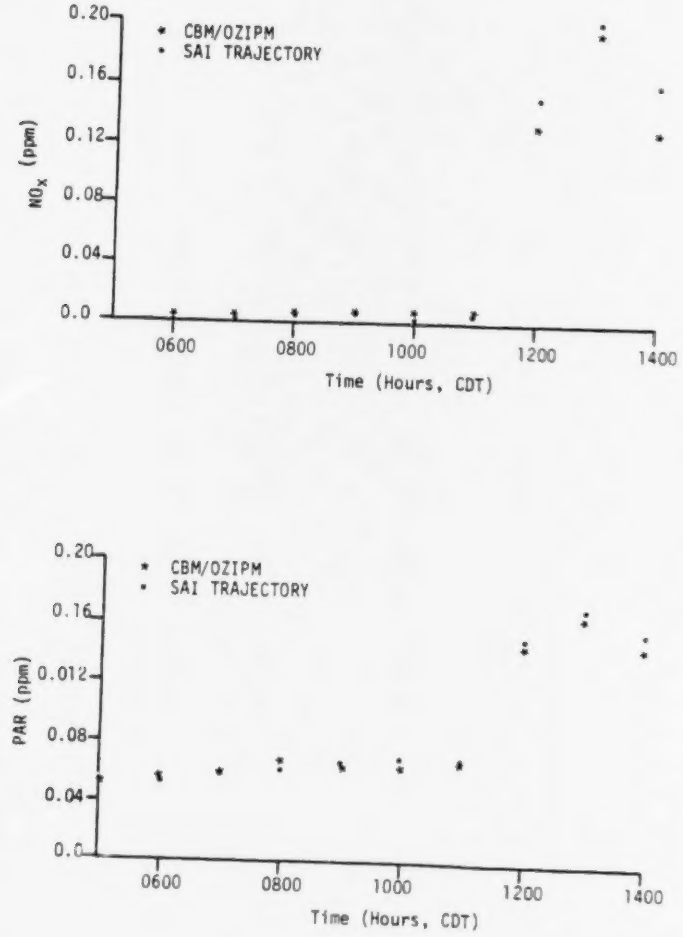
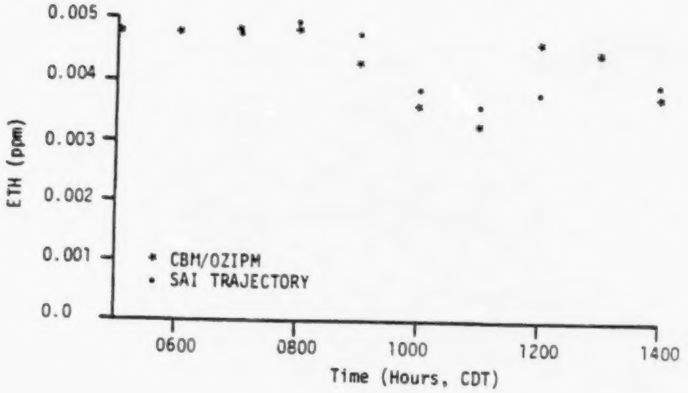


Figure 6-4. Comparison of NO_x, PAR, ETH, BZA, PAN, and O_3 for the SAI trajectory and CBM/OZIPP models for 29 July 1977.



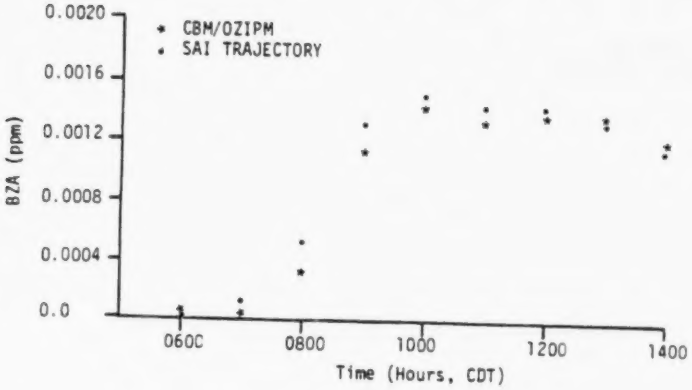
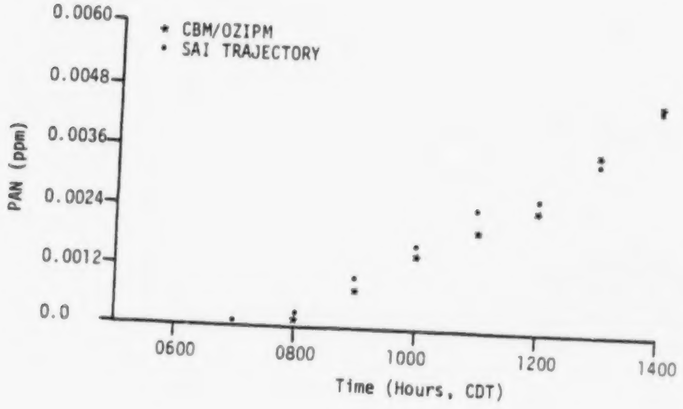


Figure 6-4. (continued)



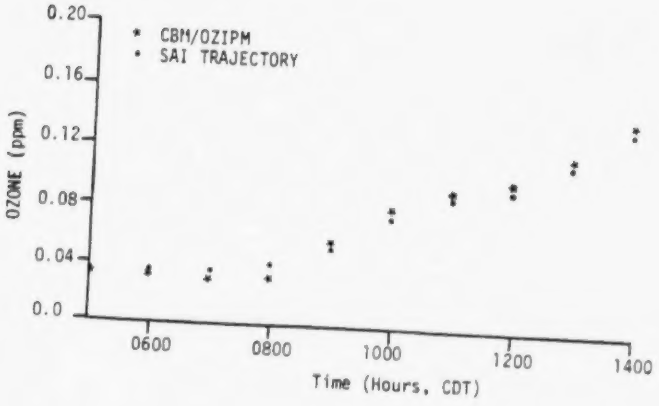


Figure 6-4. (continued)

comparison (Table 6-6) of the SAI Airshed Model and the latest Level II EKMA model, using a 30-h trajectory in Los Angeles. These results represent the maximum 1-h O_3 value estimated in the entire Los Angeles basin for a typical 1987 emissions inventory. Low background air was defined to be about 0.03 ppmC HC, 0.005 ppm NO_2, and 0.04 ppm O_3; medium background, or our best estimate of "clean" air, was taken to be 0.06 ppmC HC, 0.004 ppm NO_x, and 0.06 ppm O_3; the high background, or our upper-limit estimate for "clean" air, was about 0.18 ppmC HC, 0.005 ppm NO_x, and 0.10 ppm O_3.

TABLE 6-6. SIMULATED MAXIMUM O_3*

Model	Background Low (ppm)	 Mid (ppm)	 High (ppm)
SAI Airshed	0.124	0.194	0.273
Level II EKMA	0.125	0.190	0.295

*Future-year emissions; worst case in South Coast Air Basin: 2-day simulations.

WORKSHOP COMMENTARY

DERWENT: May I ask about this carryover of NO_x. I would think that how well you describe the behavior of PAN is quite important when you're describing the carryover. I have the distinct impression from my model that when I've got a longer radiation, most of my reactive NO_x present is PAN. How well do you think you are describing it in those various model approaches? Are you actually using peroxyacetyl radicals, or some surrogate for them, and are you thermally decomposing the PAN and those sorts of things?

WHITTEN: Yes, PAN decomposition is in the kinetics and the kinetics do follow the peroxyacetyl-type chemistry as well as we can.

We don't really have good measurements in the atmosphere to add all of the PAN's together. What measurements we do have indicate that regular PAN, peroxyacetylnitrate, is by far the largest one.

The chemistry reflects that. The chemistry is very close to the chemistry of normal PAN. We have no way of really fixing anything any better because there aren't many data from the atmosphere. But the chemistry itself is definitely modeled, thermal decomposition effects and effects of temperature, as well.

Level II EKMA, as we saw there, has a temperature that varies, the same temperature as in the airshed model. One of the reasons we put that in there is we had a hard time tracking PAN between a version of EKMA with constant temperature and the airshed model in which the temperature was variable.

DERWENT: At night the thermal decomposition shuts off, so the important period is during the afternoon. May I ask about your various grid levels in the airshed model.

WHITTEN: Yes. There are four in this version.

DERWENT: From your comparisons with EKMA, can you say if the chemistry occurs preferentially at various levels, or do you have adequate resolution really to say whether low levels or high levels are more or less important:

WHITTEN: That's an interesting question.

The airshed model set-up defines two levels within the mixing layer and two levels above the mixing layer. When I made the comparisons, hour by hour, we took the two layers in the mixing layer and averaged them together and compared that with the EKMA model results.

There can be some differences between those first two layers, say, in the morning when mixing isn't very good.

In the afternoon, the averaging is trivial in a few places when the chemistries are similar, because the concentrations are the same in those few places. The chemistry is very similar, usually.

What's happening at the third level, the one just above the mixing layer, is probably something that needs to be improved upon in the airshed model. If you look at what we see here in this 30-h trajectory, on the first day the mixing layer is going up, and the chemistry is expanding in these two layers. Then as the mixing layer comes down in the afternoon of the first day, we trap the pollutants aloft. We reenter those pollutants on the second day, which turns out to be very influential in determining what the control strategy is.

Even the airshed model treats the pollutants stored aloft in just one big layer, not a lot of little layers. How important it is to treat it as a lot of little layers instead of one big one is a research project that needs to be looked at.

McRAE: In one of the slides you showed, you compared PAN to EKMA concentrations on the entrained O_3 aloft. You had something like a 50% increase in peak O_3.

I am curious whether you have any feeling about the future of those O_3 measurements in EKMA, whether you should give consideration to --

WHITTEN: Yes. That's in our reports. I didn't go into that because of the time frame today, but that's true.

At Level II we entrained PAN and aromatic intermediates, as well as all of the various intermediate species in the Carbon Bond II mechanism. This work was the reason why the precursor reactivities are handled separately (initial, emissions, aloft, and background) in the particular version of EKMA that we have. We found that all of these things are important. In fact, we even found that PAN and CO entrainment related chemistry was responsible for a 5 to 10% effect on O_3 maximum. We had to go through and eliminate each one of these things to get to the point we finally felt confident to say that the sophisticated dispersion going on in one model didn't seem to be that important.

I think that is a fairly strong statement to make on that. I wasn't going to make it until we had gone through and eliminated the possibility that entraining PAN made a difference and that entraining these other little things made a difference. We had to eliminate all those things until we got down to the point where the only real difference between the two models you could really see were these dispersion factors, for example, eddy diffusion and two layers versus one layer.

McRAE: I have a couple other quick questions. You mentioned in your talk that EKMA doesn't include sinks in making these calculations. How important are sinks to the removal mechanism other than for O_3; how important are they for some of the other species, like PAN?

WHITTEN: PAN is not very sensitive. We did include surface sinks in the airshed model and we saw about a 5% effect.

As I said, another thing we could put into a version of EKMA is a first order dilution specific for each species to treat surface sinks.

The way this is handled in the airshed models is as a negative emission. So I looked at the algorithm, and it turned out to be in reality a first-order-dilution process. I got that first-order-dilution coefficient and put that into EKMA and then we got the difference between the two.

The biggest effect was observed at night. Ozone comes down and in the first layer of the trajectory model is essentially zero at night and yet hangs up in the second layer. However, over a 2-day period, the O_3 concentration, whether it was low or zero, was dominated by emissions.

McRAE: If you're saying that some of these secondary species are so important to what we see on the ground, would you care to comment on what kinds of measurements you need for doing future EKMA predictions?

WHITTEN: That's a very good question. The measurements aren't that important. What you have to do is be reasonable about what you are putting in the models. Think of EKMA as a main box within another box aloft. In the box aloft, you build up a certain equilibrium level of PAN, of aldehydes, and of the other species that pick up a lot of radicals and take up some activity. Now, if you just entrain the initial conditions of the box aloft again into the main box, your main box has to cook those things back up again, using up that photochemical energy. However, if you entrain PAN already in its equilibrium concentration, then you're not adding a deficit of radicals, a deficit of chemistry.

What you need to do is have measurements there of the precursors. The things you didn't measure can be generated with the model, so you're entraining a reasonable amount. It's like bringing it up to the same temperature, so it doesn't make it cold when you put it in.

McRAE: Does that suggest that the typical EKMA run should be extended in time to longer periods than what it is presently, 2-day periods?

WHITTEN: Well, for example, take San Francisco. At 8:00 o'clock in the morning it's apparently out over the ocean. And out there the standard EKMA can start at 8:00 o'clock in the morning, but the standard idea of EKMA in the middle of the city is inappropriate. This trajectory only takes about 6 h to get from downtown San Francisco to Livermore where the O_3 values are high.

In Los Angeles it can take 30 h. So fixing it at 8:00 o'clock in the morning isn't necessarily good for all cities. San Francisco and Los Angeles are two exceptions.

In Tulsa we found that 8:00 o'clock was a pretty good time to be in the middle of the city. But then you had to have the right HC:NO_x ratio.

So, we backed out of the city and started the model up there. We brought it in over the city and it generated its own HC and NO_x, depending on what the emissions were and whether there was a wind shear.

KILLUS: What is important in measuring pollutants entrained aloft is not so much that you get every single species exactly correct, but rather that you capture the overall characteristics of the air. When you go through and make various estimates of what might be considered background air, in most cases you do not have anywhere near the appropriate data to give an accurate account of the HC species. More commonly, we have an estimate as to more or less the rate at which the air will oxidize NO to NO_2, the rate at which it will convert OH radicals into HO_2, and so forth. Given those kinds of estimates, it is then possible, based on which kinetic mechanism you're using, to select a reasonable HC species to give the overall reactivity characteristics that seem correct, and also give a reactivity that does not change too rapidly with time. We certainly don't want to have the entirety of the air being entrained to be all olefins, for example, which are very reactive at the outset, then cool off pretty quickly, or all of it paraffins, which start off very unreactive and gain in reactivity.

MEYER: I'm having trouble reconciling the recommendation to initiate the model with an emissions inventory. The findings Dr. Jeffries had in St. Louis showed that the later you started the trajectory, i.e., the more up to date the initial concentrations were, the better the model performed in predicting peak O_3 concentrations.

My question boils down to if you're using emissions you're balancing an imperfect knowledge of emissions and some difficulty in figuring out when the trajectory is in the early morning hours versus the difficulty one encounters in coming up with a characteristic HC:NO_x ratio based on the ambient data, going the way that one currently goes with EKMA.

I don't know, perhaps there could be some discussion about weighing the advantages and disadvantages of these two different approaches.

WHITTEN: My feeling on the matter is that the measurements of HC to NO_x suffer in two points: (1) the instrumentation tends to be unreliable, and (2) it suffers from micromixing and micrometeorology, in that they have small pockets of HC and NO_x that are separated into different amounts in the early morning, when mixing isn't all that good. Yet, all of this stuff eventually fuses together in a horizontal sense so that by the time the 10 h passes and you generate O_3, they are all pretty well mixed.

When you're trying to measure these things at 8:00 a.m., or even 9:00 a.m., it would be crucial that you get all these little pockets of high concentration and low concentration. Even if you had perfect instruments, you might not have a sensitive control strategy which is so much affected by the measurements. The next point is that you don't really know about the nonlinear effects that occur. In fact, there are some instances where there is some influence of background concentrations. Controlling emissions by 50% may not necessarily reduce these 6:00 a.m. to 9:00 a.m. HC and NO_x concentrations. The whole premise of EKMA is based on there being at least some linear relationship between these. The crucial factor in running an emission-oriented run, if you start it early in the morning and decide that the initial concentration is background, is the actual emissions density you're going to put into the model.

The other parameter you might consider is mixing height. Since it's early in the morning, there is very little chemistry going on. So, whether you use a 50-m mixing gap or a 250-m mixing gap before 8:00, your emissions density is still the only crucial factor until 8:00 a.m. when there is a much more well defined mixing level. Whether you start out at 50 m or 250 m at say 4:00 a.m., it's not going to make any difference because the amount of the emissions is what is really important. There is no chemistry going on there.

JEFFRIES: Part of the problem is that there is a difference in the approach used by a sophisticated modeling group when it manipulates the data using intuition and a knowledge of what's going on and the approach used by, say, the Office of Air Quality Planning and Standards (OAQPS), when they are trying to propose what states are allowed to do or not allowed to do.

If you attempt to come up with a set of rules and regulations for everyone's use, as I think Dr. Lloyd said, what is the Federal Register going to say you should do to run this model? It is very difficult for someone who has never run a model to pick out the mixing height, trajectory, or emissions for a particular day and manipulate them. So, in some ways, the work we did was an effort to approximate what a smart local agency or state agency might do.

There are some bounds on the problem. You're not allowed to tweak and tune and manipulate each and every day to get the optimum fit for that day. You've got to choose one description of the meteorology or another. You're not allowed to mix everything up and see what you can come out with. Now, what you're doing mainly here is comparing one model against another model. The other model is a very super-sophisticated model that you've spent a lot of time and energy on. You didn't just make up that mixing height. You didn't go to a book and just take a number out and say, that's the mixing height today.

WHITTEN: But the point is that up until 8:00 o'clock in the morning what the mixing height is doesn't really make any difference.

JEFFRIES: It does in St. Louis, when you try to run OZIPP and you start out with 50 m mixing height and run it along a trajectory over the emissions height--

WHITTEN: That's becuase it affects emissions concentrations.

JEFFRIES: That's exactly right, and here's what happens. By starting later and later and later in the day, you're inputting initial conditions.

WHITTEN: Right.

JEFFRIES: You're inputting initial conditions instead of having to generate them by the correct description of the meteorology, emissions, and trajectory. The problem is the difference between comparing two models and comparing a model with the real world.

WHITTEN: We've tried to address real-world versus model issues for the South Coast District. We're looking into the idea of running a box model of the entire Western basin, for, say, the first 10 h to generate the initial conditions, i.e., the average trajectory over an average location for an episode day, which, for a box model, is the average conditions for that whole sector of the basin.

JEFFRIES: I think the point is that we do not have adequate descriptions, simple descriptions, of the mixing, the trajectory, and the emissions, so that a reasonably simple manual can be written to direct state agencies.

WHITTEN: Maybe you're missing the point I tried to make before. I'm saying that at 9:00 a.m., 10:00 a.m., whenever, the mixing heights can be 250 m. Before that it need only be something less than 250 m, and it needs only the emissions density defined since say 3:00 o'clock in the morning.

JEFFRIES: Yes, so?

WHITTEN: So, what I'm saying is that it's not going to make any difference if you use 50 m at 3:00 o'clock in the morning or 250 m. The concentration you end up with at 9:00 o'clock in the morning will be the same, mathematically.

JEFFRIES: How do you do that? If you run a mixing height of 50 m over a mixing surface, you come out with a very different concentration than if you run a box that is 250 m over that same emissions surface.

WHITTEN: But when you expand the box to 250 m, you end up with so many molecules, i.e., you have X number of molecules in the box at 9:00 o'clock in the morning.

Whether you put those in there at high concentration early in the morning or at low concentration early in the morning, they are still the same number of molecules in the box at 9:00 a.m..

JEFFRIES: Another problem we're dealing with here is that there are lots of EKMA models. You have already talked about at least three different EKMA models.

The models differ in very subtle ways from each other because of critical differences. There are people here who have the EPA EKMA, and if they attempt to produce some of the things you've done, they're going to get different answers.

With EKMA you've got to plug in the initial concentration and an initial mixing height, that is, a mess. You've got to come up with that somewhere.

WHITTEN: Yes, but Appendix B in the EPA guide has shown a way to handle the emissions so that the emissions density relates to the concentration that you get in the model. That would be independent then of the initial concentration.

JEFFRIES: It's impossible.

WHITTEN: That's what Gerry Gipson of EPA did in St. Louis. We'll talk about it later. I think the main thing I want to say before I sit down is that I was out to test something that a lot of people are concerned about in EKMA. That is, is the simplistic treatment of this box model compared to that of the more sophisticated model really an important factor? We have yet to find it to be important, once we know where the key trajectory is.

JEFFRIES: The message I get from you is that as long as everything in input data and so forth are the same, the answers are basically the same. The Gear method and the single-mix-layer method versus multiple layers and super-sophisticated methods don't matter very much. But the input data is going to be --

WHITTEN: All the sophisticated data necessary to run the airshed model can be used to make the EKMA model run better, too.

Secondly, you have to have the airshed model find out where the worst-case trajectory is. When you run the airshed model in Los Angeles for 1974, you get maximum O_3, say at one spot. When you change the emissions inventory for 1987, or whatever, it's someplace else.

DODGE: I think maybe this would be a good time to try to discuss the relative merits of all the models.

DIMITRIADES: Let me offer a few summary comments and see if we can perhaps start some discussion on everything that we have presented and talked about today.

You have heard from the speakers about the different methods in existence for verifying the EKMA model.

John Trijonis spoke on an approach which compares the observed impact of emissions changes with the predicted impact of emissions changes.

Since this is how we want to use EKMA to predict the impact of an emissions change, it seems that this approach is the most direct for validating or verifying EKMA.

On the other hand, there are problems. You have to select a certain HC:NO_x ratio and depend on how well it has been selected. That is an almost insurmountable problem, and I guess that constitutes a limitation of the method.

Then we heard about an approach that used a one-to-one comparison of predictions and observations of absolute O_3 air quality.

We use the concentration levels of HC:NO_x which we measure or compute from emissions rates for a given day, and then we also use data on O_3 concentrations observed on that same given day. Then we compare these observed concentrations versus the ones predicted by the model. By this approach, this comparison constitutes the basis for judging how good the EKMA model is.

Again, this sounds like a direct method for checking the accuracy of the model, but we have some problems here, too. It is highly questionable that the observed concentrations of O_3 and HC:NO_x for the same day are for the same air parcel. Because of this uncertainty, the comparison of predictions versus observations of O_3 has questionable validity.

To get around the problems of this one-to-one day-by-day comparison, investigators have offered an approach that is based on comparison of predicted frequency distributions versus observed frequency distributions of O_3 concentrations. We do circumvent the problems I mentioned earlier, but there is a question whether this comparison alone is a sufficient criterion to tell us truly how good the model is.

Finally, we heard about an approach based on comparison of EKMA with the more comprehensive AQSM's which presumably lend themselves better to verification with real-world data. That comparison is useful in some respects.

Here at EPA, we need to make a decision on which models to adopt and do further work on. After discussing the merits and limitations of the models, we would like to get some response from you.

We want to avoid discussing simply every method in terms of its good parts and bad parts and letting it go at that. We would like to put the models in some kind of order of priority or usefulness.

Also, we would like to hear some suggestions about additional research that is needed to eliminate the weaknesses of those methods. For example, do we need a new data base? Is the existing data base insufficient for one reason or another? Are the smog chamber data bases or the ambient air data bases sufficient? Perhaps a new data base is what we need against which to verify the EKMA model.

I would like to call to your attention that for the time being when we talk about EKMA, we're talking about the model, not the chemical mechanism. The subject of chemical mechanisms, how they compare among themselves, is the subject of tomorrow's discussions. Right now we would like to concentrate on those methods that you have heard for verifying EKMA. If at all possible, we'd like to get some reaction in terms of which one is the one we should stay away from; which ones we should concentrate on, etc.

Would any one of the speakers like to offer to speak first?

WHITTEN: I have a relatively minor point to bring up first, but it is something I feel strongly about. I think that a crucial point in EKMA is relating the HC and NO_x, both concentrations and ratios, that you have to use in the model to the ambient data.

Now I have suggested an alternate method that makes the model relate to ambient emissions, since that is what you want to control. But that, of course, also has weaknesses. So what I suggest is that we need data to verify the HC:NO_x ratio more significantly. It may be like a van that moves around in a 2- to 4-km^2 area to get an integrated value of the 6:00 a.m. to 9:00 a.m. HC concentrations.

I think there is so much fluctuation in the 6:00 a.m. to 9:00 a.m. data we get from fixed monitoring sites, that it makes the whole use of them very questionable.

That is one of the reasons I went to the emissions idea, because it becomes much more stable; it only changes when you change the emissions.

I think it's possible, since the Australians were able to, to put HC and NO_x instrumentation in vans and get an integrated concentration in the downtown area, then find out whether these fluctuations disappear if you measure HC over a grid square, rather than just a single point. I think gathering those data is important.

If it turns out that what's being measured across the nation right now at individual stations correlates extremely well and you do see the same amount of fluctuations in a van as you do at a single site, maybe it's a realistic effect.

TRIJONIS: What is a realistic effect?

WHITTEN: These wide fluctuations that you get from day to day. As Dr. Jeffries and Dr. Martinez observed, very large differences in 6:00 a.m. to 9:00 a.m. --

TRIJONIS: They aren't spatially homogeneous. I've been doing a study for the Air Resources Board correlating NMHC:NO_x ratios at five or six sites in Los Angeles, and they don't correlate at all.

WHITTEN: Yes, but those sites are separated by 10 mi or more. I'm talking about within a 5-mi square, something you would think of as an air parcel that's going to end up as the maximum O_3.

TRIJONIS: There's always the possibility --

WHITTEN: In that square, is it uniform?

TRIJONIS: There's always the possibility of data quality artifacts. The ratio could be fairly uniform from day to day, and the variation you see be a data quality problem.

WHITTEN: That's another problem, but eventually you're going to come to a point where you've got perfect instrumentation.

JEFFRIES: I don't think you can pass it off as a data quality problem.

TRIJONIS: I didn't say it was, but there is a possibility it is.

JEFFRIES: There are a lot of problems with HC instruments, and that's been true historically. That's one of the problems that was dealt with when the only data base we have that's worth looking at for testing EKMA was developed. You have to consider that what was measured back then versus what's measured now is not necessarily the same thing at all. The Australians had one HC instrument and one NO_x instrument. They still saw the same kind of variations and distributions. The pollutants are simply not spatially or temporally homogeneous. The air parcels don't come from the same places, and they pass over different sources with different characteristics and end up with mixtures of source contributions. The Australians actually had 30 HC species, 500 to 600 samples, and source reconciliations on graph samples from all over the place. They can tell you that the composition in this parcel had so much automobile exhaust, so much evaporant, so much from solvents, etc. --

There is a tremendous variation, depending on where that actual air parcel came from.

As times goes on and they mix more and more, sure, they'll become more homogeneous.

TRIJONIS: The model relates to that homogeneous average.

JEFFRIES: In terms of the initial input conditions, to use it in the way that it has to --

TRIJONIS: Then you take that one little point that's being measured and you're saying that that's the average.

JEFFRIES: That's a weakness in EKMA. The technique that both Dr. Martinez and I have used is one which considers the whole distribution. You've got to go to the whole distribution. You can't talk about a single point. The single point doesn't represent anything but that one number, that measurement.

What does a mean HC:NO_x ratio mean in a case like RAPS data where the stuff is spread all over the whole axis?

WHITTEN: I showed the same thing in Tulsa. You see various --

JEFFRIES: I'll bet in the airshed model every square is different from every other square. When you do these comparisons between EKMA and the airshed model, how do you go from an airshed model number which has all the spatial numbers you need in the input to a single number that gives you the EKMA?

WHITTEN: That's why we went to the emission-oriented one, so that we would go back far enough in time so that out in the ocean they're all the same. Aren't they?

MARTINEZ: I think that asking for more data at this point simply postpones the decision on the issue for about 5 or 6 years. It's always a good thing to do. The more you know, the better off you are. But, we are faced with fairly short-term decisions, and I disagree with Dr. Whitten on that. We are stuck with certain kinds of data, good or bad, that's what we have.

That was part of my motivation in going the way I went with the EKMA approach. I thought, we have data and we have O_3 measurements, and we have to make some decisions in the immediate future. Using the model, perhaps these data aren't so bad after all. How well can we do? Once we know how well or how poorly we can do, what can we do about it? You have to consider the approach that I suggested, which is similar to Dr. Jeffries' from that point of view.

Then, for the ultimate application, the numbers and distributions are of no use unless you plan to use them, and that's where the two possible applications that I discussed come in. Basically, you're trying to improve on your predictions, and you're doing it within the framework of the available data.

DIMITRIADES: So what you are saying is with the data base that is presently available, this is what you recommend as being the approach?

MARTINEZ: I don't want to say that this is the best possible way in all the world, no. It's just one way that, considering the imperfections of the data and the model, allows you to take into account your answer.

DIMITRIADES: I don't disagree with that, but we are going to do additional work in our efforts to get an improved model. In view of this, would you propose another method if we were to get another data base?

MARTINEZ: Given that we cannot get perfect data and we cannot get a perfect model, then that approach also applies to any other model and any other data base you can come up with.

So does Dr. Jeffries', for that matter; and so probably do the others. What I want to stress is that I do not mean to imply that once we apply EKMA in this fashion, then that's your answer and then that's it. The EKMA model gives you an answer that should be checked. It doesn't tell you how the value you chose gave you the HC and NO_x that you put into a model in the first place. That's for you to decide.

There are other methods that optimize the cost of all these strategies. That is another factor that you can throw into the pot.

Running airshed models is a time-consuming, rather expensive process, compared to these simple models. I propose that the simple models be run first, to look at your strategies.

In light of Dr. Whitten's comparisons, maybe you will not be that far off. But, if you really want to be sure, then once you've selected your control strategies, you screen them, pick the ones that seem to work best, and check them against the big models.

I am troubled by Dr. Whitten's remark that neither the chemistry nor the dispersion matter very much.

WHITTEN: I didn't say that.

MARTINEZ: What matters?

JEFFRIES: The input.

WHITTEN: No, I didn't say that. I didn't mean to say that.

MARTINEZ: My point is that it seems that both the simpler models can give an account of your uncertainties. The complex models, with their uncertainties; one leads into the other.

TRIJONIS: I think the strong point of Dr. Martinez's and Dr. Jeffries' work is the use of a distribution of the ratios rather than a median ratio. I think it's really not a "validation" to try to validate EKMA in an absolute sense. It's intended to be used in the end to evaluate emissions changes, so you want to evaluate it in a relative sense. I think that's where the strength of Dr. Whitten's and my own work is. We look at historical emissions changes and see how EKMA performs historically. Dr. Whitten can do that by seeing how EKMA performs under emissions changes and how a more sophisticated model does under emissions changes.

So possibly we could combine the two strengths and do future studies either with historical trend analysis or by comparing EKMA to other types of models. When those studies are done we should not use the median ratio approach but rather the distribution-type approach. We might use a normal distribution of ratios. Using that we could then make comparisons, either with historical data or with results from a more sophisticated model.

DIMITRIADES: Do you have enough historical data to allow you to arrive at distributions?

TRIJONIS: The distribution is fairly well known. That would not be a problem. However, instead of taking one point on the EKMA model and tracing that through time, you'd take a distribution of points and trace the distribution through time. I think that could be done.

ESCHENROEDER: So you're saying that the work breaks down into two parts. One is working on models and their improvement; the other is using these models in the statistical framework once they are developed to play the distribution game.

TRIJONIS: Right. I wouldn't go with only the distribution game, in looking at that in an absolute sense, because that's not at all doing a verification study. I think Mr. Gipson in one of his first slides made that point.

ESCHENROEDER: Both Dr. Martinez's and Dr. Jeffries' work depends on the model as a starting point in their scheme, in their logic, and that that is used as a tool to do a statistical study of different sorts on an existing body of data.

TRIJONIS: Right.

ESCHENROEDER: What you're saying is we can sharpen the tool but we should also be trying to apply it as a tool for making decisions in an uncertain environment because it's always going to be uncertain to some extent. As we narrow our uncertainties, the model is going to be accordingly narrowed. However, you should start out with the best model you can on an absolute basis.

TRIJONIS: Right, but it should be tested under changing emissions conditions, either by historical comparison or by comparison to changing emissions with the SAI model.

ESCHENROEDER: Try to get as much dynamic range as you can?

TRIJONIS: Right.

ESCHENROEDER: Even if it's going from one morning to another. I know that's not turning the emissions up and down, but that's all we have for varying morning ratios for HC and NO_x.

WHITTEN: About the only change in emissions, really, that you have, is weekday to weekends.

ROMANOVSKY: I wonder about the wisdom of taking distributions as regards concentrations and the ratio. If you take the distribution of the O_3 and average it out, you find we don't have a big problem, not even in Los Angeles.

TRIJONIS: The distribution of what?

ROMANOVSKY: The distribution of the peak O_3 values over a period of a year. If you take the distribution of O_3 and average it out, then you dont' have very much of a problem, not the kind of problem that control agencies have to address.

I'm wondering if we shouldn't be looking at worst-case scenarios as opposed to distribution.

TRIJONIS: If you take the entire distribution, you're taking the mean. If you address the entire distribution, you can very easily address worst-case situations. You can ask the question, what's the worst first percentile, fifth percentile, tenth percentile, what's the mean. You should address the entire distribution, not just the mean of the distribution.

ROMANOVSKY: You should make sure that the data you use in regard to the product pertain or relate to the appropriate data for the precursors.

TRIJONIS: I guess that's where Dr. Jeffries' model comes in, where it matches the two.

DIMITRIADES: If you want to combine the two approaches as you suggest, don't you have to have an adequate data base for 1964 and 1965 that will allow you to construct the frequency distribution of O_3, HC, and NO_x at that time?

TRIJONIS: Yes, you could run the model in 1965, essentially, that's right.

DIMITRIADES: You have the data base?

TRIJONIS: Yes, for Los Angeles.

JEFFRIES: Then you'd do it for the next 3-year period, and the next 3-year period, and the next 3-year period.

DIMITRIADES: Yes, as long as you have the data --

TRIJONIS: I think you'd do it for 1965, and then make predictions of what happens to that distribution in subsequent years. You only do it once, then you predict what that distribution is for every subsequent 3-year period based on the emissions changes.

JEFFRIES: But, there is also an alternative to that. Other things like meteorology over the 5-year or 3-year period might influence the shape of the diagram. So, you would fit the frequency distributions for each year and compare the isopleth diagrams to see if the distributions remain stable or change, and if they change whether they change in a way that reflects the underlying changes in the meteorology over a longer time period.

TRIJONIS: How well could EKMA predict, starting in 1965 to 1972, a 50th-percentile O_3 level?

I think you would want to start with only 1965 data and your emissions changes that answer that question. You would be answering a slightly different question, I think, than the one I was thinking of.

JEFFRIES: The difference is that the isopleth diagram derived from the 1965 data incorporates the meteorology for 1965.

TRIJONIS: Right. Well, then you would incorporate 3 years of meteorology. It could differ slightly from the 1972 to 1974 meteorology, but that would be one of the reasons for the disagreement. I don't think you ought to force-fit them. You ought to see; what you predict should be the distribution of O_3 in 1975 for 1975 to 1978 what is the actual -- yes, that could be done, that's true.

DIMITRIADES: I guess what I was asking was whether quality data are available. Aren't there questions about the entire $HC:NO_x$ data base?

TRIJONIS: No more than for present data. There has been a calibration problem for NO_x for a long time, but that's like a 17% error. It's a constant type of error.

The HC data and the nonmethane hydrocarbon (NMHC) data for Los Angeles are essentially worthless. The total hydrocarbon (THC) data are somewhat better, and all we use is THC, using an empirical formula to calculate NMHC from that. They aren't as good as, say, the NO_x, CO, or O_3 data. If you correlate O_3 levels from site to site and then look at what the correlation goes up to as the sites tend to get closer (the closest sites are within 3-4 mi of each other), and you do the extrapolation on the 0.0 mi for O_3, you get a correlation of about 0.85. For NO_x and CO you get a correlation of about 0.75. For THC it goes down to about 0.60 or 0.65. That's the worst. If you go to NMHC, it goes down to about 0.3. So those data are really worthless. The THC data are not as good as the O_3, NO_x, or CO data, but they contain some information.

DIMITRIADES: I can see the advantages of combining the two approaches provided we have adequate data to do so.

I have some questions about that approach alone, whether the data for frequency distributions alone are adequate criteria for judging the performance of the EKMA model.

TRIJONIS: My one point is that that doesn't change, that doesn't test the model under changing emissions, which Dr. Romanovsky, Dr. Whitten, and I think is important.

JEFFRIES: The method is not meant for validating the EKMA model. It is a different method altogether. There is a method for using ambient data in an isopleth diagram. It is different.

The isopleth diagram can come from a hundred different places. I just happened to show one way to get it.

What is implied in the method, though, is that over some time period in an urban area there is a single isopleth diagram that adequately captures the essence of the O_3 precursor relationship. That's all it says.

So far, in two different cities, over two different time periods, it has been proven possible to derive a diagram so that that relationship holds.

DIMITRIADES: It sounds like being empirical.

JEFFRIES: In many ways it is. It's an engineering answer in one sense. You can provide all kinds of kinetic underpinning, but when you come down to it, it is merely a transfer function for converting precursor distributions into O_3 distributions. That is the problem with it.

It doesn't have the kind of cause-effect relationship you can point to in the model, where you can say, this chemistry does this, and the wind blew it from here to there, and it made that. It can't do that.

ESCHENROEDER: I think you're selling it short, because embedded in that technique, as you pointed out, is a model that has a lot of coefficients, B, C, N, each of which is identifiable with some phenomenological thing that--

JEFFRIES: Absolutely.

ESCHENROEDER: So there's some underlying truth to it in a deterministic sense, to begin with, or you wouldn't have gotten to the answer as fast as you did.

JEFFRIES: That's correct. In a sense we didn't have those parameters totally free as they've been described by Dr. Trijonis; the parameters are quite restrained.

ESCHENROEDER: Absolutely.

JEFFRIES: We could have done the whole thing with one parameter, C. That's it. In fact, what you could do with the data he showed on the board is take the highest point up there and the highest O_3 concentration and figure out what you have to multiply by to get that value to come out right, and that's it. That's the C. You can then plug it back in and come out with the frequency distribution. I'm going to take the Houston Area Oxidant Study (HAOS) data and run through it very quickly and try it out. The weakness I see in the method is that it's very data-dependent. You have to have HC and NO_x values that are reasonable representations of the frequency distributions of measured values in the city, and you have to have enough O_3 stations to know that you've got a reasonable representation of the O_3. So, in that sense, the weakness of the method is that it's simply data-dependent.

MARTINEZ: There is a small problem, also, with fitting the whole distribution on that. You're really interested in the distribution. And the least-squares method that considers the whole distribution spends most of its time fitting the part of the distribution that doesn't really interest you that much.

JEFFRIES: We found out very quickly that we could take a frequency distribution printout and an isopleth, and looking at a few points, we could figure out what the thing was going to be. So you don't have to have it fit the whole distribution; you can optimize to fit at one end or the other end or in the middle or wherever you want it.

WHITTEN: I think that part of what Dr. Jeffries says is probably true, that it's a way of mapping the frequency distribution of concentrations of precursors to O_3 generated. However, I would add, and this is the thing that for me is very different, at constant emissions.

Because, basically, the emissions of all of these data are constant. What we are looking for is a model that relates emissions and the control of those emissions to the generation of O_3.

I don't think Dr. Jeffries' model does that. I don't think it relates fluctuations in the concentration you see due to meteorology or other effects -- the fact that automobiles are driving around differently one day or whatever -- to change in emissions. I don't think that's been demonstrated; that emissions, which are what we're all trying to get to, are supposed to be HC-control methodology.

JEFFRIES: A clear assumption in the model is that there is a linear relationship between emissions and concentrations.

WHITTEN: Not in the way you've used the model.

KILLUS: I'd like to point out that this sort of historical trend analysis Dr. Trijonis has been discussing is one of the very few methodologies we have that independently verifies our emissions data base. One of the nightmares modelers have is that they seldom have any sort of control on inputs. What do you do if, for example, the emissions data given are incorrect?

What does EKMA do, for example, if it is depended on and the control strategies are totally incorrect. Obviously, all the models and all the control strategies break down under those circumstances. Historical trend analyses, on the other hand, are one way of getting an estimate of whether one can believe that control strategies have been effective, and by implication, whether there is any likelihood they're going to be effective in the future.

WHITTEN: I'd like to bring up another point. I think something that's been left out of the central discussion here is the method given in the EPA guidelines for Level III. That method tries to address, to a certain extent, the statistical problem in O_3 distribution by taking the five, or however many, highest days and doing a separate city-specific Level III trajectory for each of those days. It then does controls on each day. I think that is more related to solving the problem than looking at frequency distributions or fluctuations and assuming that a poor model will generate a poor distribution. A good distribution from a poor model seems possible to me.

I would be more comfortable in terms of Dr. Martinez's problem, i.e., the problem of working with what we have, to stick with Level III guidelines as they are. To me that's a more satisfying methodology for handling the statistics.

JEFFRIES: The problem with that is that you end up deriving a control for a point that in the future is no longer the point of concern, and the airshed model automatically switches and produces more O_3 someplace else in the future.

WHITTEN: But that's a problem you have to live with when you're looking at trajectory versus isopleth-grid-model sets. If you can't afford a grid model the next best thing is some sort of trajectory, and you have to live with that uncertainty.

JEFFRIES: Even so, with the airshed model, how do you relate that to the O_3 standard? The O_3 standard says that it's site-oriented and the airshed model is predicting the concentrations of each grid. Do you base your control strategy to meet the O_3 standard at each individual grid or do you base your strategies to meet them just at the sites? That's a whole other question.

WHITTEN: That's another workshop.

ESCHENROEDER: We're still at the meteorology of that particular design day. It may not produce the worst case for the new emissions pattern at a future time.

CARTER: So far it never has in the airshed model.

What Dr. Whitten was referring to with the city-specific EKMA guidelines, I think, is that we did look at, say, the 5 highest days that give a high O_3 concentration at any particular site and then tried to model one of those days. I think the EKMA model at least does predict that the control requirements do not decrease monotonically with O_3 values.

But using the design O_3 level from the design value approach with some sort of isopleth diagram may not be appropriate. You do have to consider day-specific type situations. Now, with the city-specific guidance, we're doing it in a very brute-force approach. We're considering 5 days. To do it completely, you would look at all days above the standard.

McRAE: Dr. Romanovsky, I'd like to ask you, and perhaps Dr. Whitten whether you would like to comment on the question. Do you have any feeling about whether the worst days are in fact the toughest ones to control?

Some of the things that are coming out of multiday runs and the kinds of things that Dr. Whitten has been doing make me very nervous about the levels of controls that we developed on the basis of the 5 worst days, providing a guarantee that it will generate levels below the standard on no other days.

Do you have any feelings about the choice of statistics and whether, in fact, it will achieve the goal you want to see?

CARTER: I think with a specific model like city-specific EKMA, you can pretty much predict which days are going to be the toughest; that's the control and that's the one with the highest background levels.

You don't reduce the background levels at all, or you reduce them only a moderate amount. That just means the city has to implement greater control.

I think that's being demonstrated with the airshed model, too. Some of the results we've seen in St. Louis are very day-specific, e.g., the change in O_3 with reduction of HC. And, of course, that's going to be influenced by the boundary. So what does that mean? It means that in terms of the control strategy developed, the change in boundary conditions is going to be a critical factor, and not only to the modeling analysis itself.

I don't know if I answered your question, but I can't see it being appropriate simply to pick a high O_3 day or a few high O_3 days, do a modeling analysis, and determine what the controls are.

I think you should look over a wider range of the distribution. How far you'd have to go, I don't know.

MEYER: One pertinent comment to that, Dr. Carter, is that for many cities (not Los Angeles, but many cities), if you look at the 5 highest O_3 days, the distribution tends to tail off fairly rapidly after that. There is frequently a fairly substantial difference for a lot of cities after you've looked at the 4 or 5 days.

MARTINEZ: One problem with the Level III approach is that new chemical models can bring another joker, so to speak. Which model do you choose? Dr. Jeffries will show you tomorrow that he can play a game that you can choose the model that gives you the results you want. That is something to be considered in the whole EKMA selection process. Thus, the trend analysis perhaps ought also to be done for the other models to see how they do.

My work has shown that they are quite different in their capabilities, so that you may select one over another, depending on what part of the HC:NO_x plane you are in.

I'm not sure how Dr. Jeffries' work addresses that problem. I suspect that if you have an isopleth surface for any model, you'll be able to fit it fairly well.

JEFFRIES: I'll just change all the parameters so that they all look the same anyway.

KELLY: I'd like to ask a practical question. For most cities where this may be applied, like Detroit or Cleveland, where they have O_3 exceeding the standard, there haven't been any NMHC measurements for a long time. The only measurements that have been made are the SIP measurements made last summer for 3 months with one HC monitor.

JEFFRIES: Missouri has 3 days' total nonmethane hydrocarbon (TNMHC).

KELLY: What do you do in that case? In Detroit we did not find this wide variation; from 6:00 a.m. to 9:00 a.m.. I think we found a ratio like 4 or 5 to 1, plus or minus 1. This is at one site, using a very modern NMHC analyzer, one that measures NMHC chromatographically.

We did find a very stable ratio. If what you say is true and the micrometeorology influences the ratio, it's going to be used for this whole city, and it might not be representative.

MEYER: Let me ask, was that ratio integrated over 3 h? I'm wondering if part of the explanation for this isn't the temporal integration that comes into play here.

For example, one might expect to find a great deal more variability if one looks at 30-min average concentrations or hourly average concentrations, as opposed to 3-h average concentrations. I wonder if it's been people's experience to find that some of these differences get smoothed out over longer sampling periods. Does anybody have any experience in that regard?

BUFALINI: I think I'm inclined to agree with you. I'm amazed at the difference in the HC:NO_x ratios that have been presented. I don't recall seeing that high a ratio when going through some sort of integration, an hour or longer. One wonders whether there is a puff of HC coming in to give you a full 100:1 ratio.

The 0.9 seems more reasonable with auto exhaust when someone is monitoring right behind a tailpipe. I think in general one does not observe those high ratios over a period of time.

KELLY: The criterion at the site of the HC and NO_x we use is to get so many meters off the road, based on traffic, and --

UNIDENTIFIED SPEAKER: Presumably the HC monitors are sited in the summer so that they avoid any one dominant source; they may be near a road and be down at the exhaust, but not on the tailpipe. You're measuring a couple of ppmC at 6:00 a.m. to 9:00 a.m., or something like that.

JEFFRIES: I think it has a lot to do with identification of large point sources of HC here where the monitor might be. But with these kinds of variations, either the automobile HC:NO_x ratio is varying greatly or most of the influence we're seeing is due to point sources of one or the other.

TRIJONIS: There is a more important factor, actually, which is carryover. The greater the age of the air mass, the more HC:NO_x-enriched it is. In fact, in the afternoon the ratio goes up to 100:200 sometimes, because the NO_x go away while the HC's stick around.

So, rather than the specific source area you go to, it's probably the amount of carryover you have from yesterday that determines the day-to-day variation in your ratio. If you have more carryover, you have a higher ratio.

KELLY: I don't think that happens in the Detroit area. General Motors, in the urban core measured HC and NO_x, using our mobile laboratory and our HC upwind monitor, as well as two monitors from EPA, one of which they set up in the city all summer, and one of which they set upwind of the city. We thought the upwind site would show more HC's, but the upwind site didn't see any HC's. Our HC upwind monitor used the total-minus-methane technique which presumably isn't reliable unless you get up above 0.5 ppmC. But there wasn't any evidence of transport of HC's into Detroit.

I don't know about Los Angeles or other places where you have a lot of stagnation, but in the Detroit area, downwind or in the afternoon, your HC levels fall off dramatically down to tenths of ppmC, and NO_x levels fall down to 5, 10, 20 ppb. However, in the morning you do see a big peak from 6:00 a.m. to 9:00 a.m. That's what you're measuring, and presumably that can photolyze and form the O_3 downwind.

But, my question was that with all this controversy over ratios and using distributions, well, that may be all right if you have a lot of data, but what if you have 3 months worth of data, and --

JEFFRIES: Three days.

KELLY: -- and you must come up with a ratio to use in this model to predict controls?

WHITTEN: There is another aspect to this idea of the $HC:NO_x$ ratio that Dr. Bufalini touched on, namely, if you use more and more days to average your $HC:NO_x$ ratio, it zeros in on this nice, solid number. On the other hand, you're trying to predict a very specific episode date for the O_3, so you're only looking for one especially bad day. So, on the one hand, you're averaging things over a lot of days to get this $HC:NO_x$ ratio that is extremely critical to your control strategy, and, on the other hand, the whole thing is an episode day and it is very difficult to get data for that day.

I have a lot of reservations about the current EKMA with the HC and NO_x.

That's one of the reasons I went and worked on this emission-oriented idea where you start upwind from the city where the initial condition is low and use an emissions inventory to generate the isopleth diagram. The abscissa in the diagram is relative to emissions, and it doesn't relate to an initial concentration.

JEFFRIES: You're substituting knowledge of emissions for knowledge of the $HC:NO_x$ ratio.

WHITTEN: Definitely.

KILLUS: But, you have to have the knowledge of the emissions anyway, or the control strategies couldn't be effective.

JEFFRIES: No, you don't. You have to assume that there is a relationship between emissions and ambient concentrations, that's all.

KELLY: It doesn't seem to me that emissions can give you HC's and NO_x. At least they can't in the threat area. You don't really know what those emissions are, specific HC's, so you don't know what the ppmC is of those emissions.

You know tons of organic compounds and tons of NO_x; what does that give you in terms of ratios?

WHITTEN: If you know the tons then you use that to generate the concentrations, it's very simple.

JEFFRIES: Assuming splits and --

TRIJONIS: Even if we know that, the ambient ratio is about three to four times as high as the emissions ratio, and because of the short-lived nature of NO_x, you can measure tailpipe emissions until you get the right emissions ratio, and 1-h or 2-h or 3 h later it starts going down. Or, if you have some carryover from the previous day, you have an ambient ratio of about two to four times the emissions ratio. That's why I distrust just using the emissions data. Those data might not be representative of the real ambient ratio and the real ambient reactivity, unless you have something that will destroy NO_x in your model.

WHITTEN: That's the point. You start the model at 4:00 o'clock in the morning or 2:00 o'clock in the morning, and by 9:00 o'clock in the morning a lot of NO_x are already destroyed. So you do see a higher ratio in the model already, much higher than the emissions ratio.

I'm just saying that I feel there are certain advantages. They both have disadvantages, but I think there are certain advantages of the emission-oriented EKMA over the initial-conditions HC:NO_x ambient measurement method.

You can always check the emission-oriented EKMA. If the model predicts at 9:00 o'clock in the morning that the HC:NO_x ratio is such and such and the concentrations are such and such, and if they are an order of magnitude off, then you think maybe something's wrong with the model. You have a check on it. You don't lose that. You don't need those numbers. You don't depend on HC and NO_x measurements.

7. DERIVING EMPIRICAL KINETIC MODELING APPROACH ISOPLETHS FROM EXPERIMENTAL DATA: THE LOS ANGELES CAPTIVE-AIR STUDY

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ABSTRACT

Under the sponsorship of the Coordinating Research Council, Environmental Research and Technology, Inc. conducted a series of captive-air experiments in support of photochemical kinetic model validation and Environmental Kinetic Modeling Approach (EKMA) evaluation. Captive-air experiments are described which were conducted over approximately a 7-week period from September to November 1981. Sunlight irradiations were carried out in a large (100-m^3) and four smaller (4-m^3) satellite Teflon chambers. The facility was located on the roof of a building on the campus of the University of Southern California in Los Angeles. Species measured included nitric oxide, nitrous oxide, ozone, peroxyacetylnitrate, nitric acid, individual hydrocarbons, and individual aldehydes. Subequent data analysis is discussed in which the data are compared with the Ozone Isopleth Plotting Package diagram derived from the EKMA model constructed for Los Angeles during October 1981. The model employed both the standard-EKMA chemistry and the Environmental Research and Technology, Inc. chemical mechanism.

INTRODUCTION

Control of ambient ozone (O_3) concentrations in urban and rural areas of the United States is of continuing concern to regulatory agencies. The fact that 33 areas of the country have applied for a 5-year extension of the date for attainment of the National Ambient Air Quality Standard (NAAQS) for O_3 (Federal Register, 1981) illustrates the magnitude of the problem. The reduction in ambient concentrations of O_3 requires control of the precursors, oxides of nitrogen (NO_x) and hydrocarbons (HC's), which undergo a complex series of sunlight-initiated reactions in the atmosphere. The U.S. Environmental Protection Agency (EPA) developed the Empirical Kinetic Modeling Approach (EKMA) to calculate the precursor reductions needed to achieve the NAAQS for O_3. EKMA has been described described fully elsewhere (Dodge, 1977; Whitten and Hogo, 1978; EPA, 1981) and was used for many of the 1979 State Implementation Plan (SIP) submissions.

While EKMA is a significant improvement over the Appendix J approach (Dimitriades, 1977), it has its own shortcomings (no spatial resolution of emissions, similar treatment of ground-level and elevated emissions sources, assumption of fixed reactivity for the HC mix regardless of the geographic location). The EPA recognized the need for a more sophisticated model for those areas of the country most heavily impacted by high levels of O_3. For such areas, EPA proposed (Federal Register, 1980) that photochemical air quality simulation models should be applied, since they treat emissions, meteorology, chemistry, and their interrelationships in a more realistic way than does EKMA. However, largely because of the concern expressed by the states that the data requirements for these models were substantial, costly, and would be unavailable for the 1982 SIP revision submittals, EPA decided to recommend that the city-specific version of EKMA be applied nationally. Because the EKMA methodology relies heavily on a chemical approach to reducing ambient levels of O_3, it is important that the chemistry and its use in EKMA be examined in detail before enormous financial resources are committed to following a control strategy dictated by the results of EKMA.

Several workers have questioned the adequacy of the standard chemical mechanism used in EKMA to describe atmospheric reactions under a variety of conditions (Hayes et al., 1980; Carter et al., 1982). Hayes et al. (1980) evaluated the sensitivity of the EKMA analysis to the chemical mechanism employed as part of an overall evaluation of EKMA to the control of O_3 and (nitrogen dioxide (NO_2) in the South Coast Air Basin in California. They employed two chemical mechanisms, the standard-EKMA chemistry (Dodge, 1977) and the carbon-bond chemistry (Whitten, Killus, and Hogo, 1980), and found significant differences in the control requirements for each case.

Carter et al. (1982), using indoor smog chamber data, assessed the impact of the chemical mechanism employed and of the initial levels of precursors (including nitrous acid and aldehydes) on the shape of the O_3 isopleths in EKMA. They concluded that the shapes of the isopleths, and thus the HC control requirements, are significantly influenced by the aldehyde content and by the chemical mechanism employed. Other workers have recently obtained results based on different chemical mechanisms and have reached similar conclusions (Jeffries et al., 1981; Martinez et al., 1981).

The objective of this study was to obtain experimental data in a captive-air facility in the Los Angeles basin. Los Angeles was selected because of the severity of photochemical smog and because of the number of air monitors within the basin. Ambient air, captured in the early morning hours (between 6 and 9 a.m.), was subjected to sunlight irradiation in Teflon chambers, and the maximum O_3 formed each day was plotted as a function of initial HC and NO_x. These results are being compared with EKMA isopleths generated specifically for the Los Angeles area for October 1981, under the EPA guidelines for EKMA.

This paper describes the experimental data collection and the methodologies employed for data reduction and for the comparison of experimental data with the results of EKMA calculations. The experimental data are currently being reduced and validated, and full results of the program are expected to be available in early 1982.

EXPERIMENTAL DESIGN

Captive-air experiments were conducted for approximately 7 weeks from September to November, 1981. The facility was located on the roof of the Gerontology building on the campus of the University of Southern California (USC). Sunlight irradiations were carried out in a large (approximately

(100-m^3) and four smaller (4-m^3) satellite Teflon chambers. All chambers were inflated with ambient air between 6 and 9 a.m. Initial concentrations measured included nitric oxide (NO), NO_2, O_3, and peroxyacetylnitrate (PAN) (all chambers), individual HC's and individual aldehydes (large chamber), and total nonmethane hydrocarbon (NMHC) (satellite chambers). Light-molecular-weight HC's were measured on-site by gas chromatography (GC). Heavier HC's and aldehydes were measured by GC and by high-performance liquid chromatography (HPLC), respectively, upon return of the samples to Environmental Research and Technology's (ERT's) Westlake Village laboratory according to the methods described below. Aldehydes measured included formaldehyde, acetaldehyde, benzaldehyde, and any C_3 to C_7 aliphatic aldehydes present at detectable concentrations (typically 1 to 2 ppb) in the samples.

Before exposure to sunlight, additional amounts of NO_x (50, 100, and 200 ppb, respectively) were injected into three of the four satellite chambers. This approach provided a cost-effective way to generate four points on the NO_x-NMHC-O_3 isopleth diagrams for each run (i.e., four HC:NO_x ratios for each initial HC level). This protocol also provided a built-in daily control between the large chamber and one smaller satellite chamber to which no NO_x were added. Because of the significant difference in surface-to-volume ratios, any significant discrepancy between the results obtained in the large chamber and those obtained in the smaller satellite chamber may be indicative of wall effects. Selected dilution experiments were also carried out. After injection of NO_x in the satellite chambers, all black covers were removed and sunlight irradiatiions were carried out for approximately 6 h. Measurements also were made of temperature, relative humidity, and solar ultraviolet radiation intensity.

Description of the Chamber Facility

The large outdoor chamber is constructed from 12 panels of FEP Type A Teflon film, each 30 ft x 48 in x 0.002 in. The panels are heat-sealed together and the seams are externally reinforced with Mylar tape. Teflon was selected because of its excellent transmission of actinic ultraviolet light (295 to 400 nm), its low permeability, and its chemical inertness. The small chambers were also made of Type A Teflon film.

The large pillow-shaped Teflon chamber is supported by a net and by ropes running across a steel pipe frame 2 ft above the roof to allow air circulation under the chamber. The chamber is covered by a black plastic sheet during filling, injection, and mixing procedures before irradiation. The chamber has two ports for the introduction of air and reactants and for sampling of gaseous and particulate products and reactants, as well as for flushing and dilution. Monitoring instruments are connected to each chamber compartment via Teflon lines and Pyrex manifolds.

Measurement Methods

Aldehydes were measured by sampling the matrix air with microimpingers containing an aqueous solution of the reagent 2,4-dinitrophenylhydrazine

(DNPH) (Grosjean et al., 1980; Fung and Grosjean, 1981). DNPH reacts specifically with carbonyl compounds to form hydrazone derivatives, which are extracted by selected organic solvents and separated by HPLC using reversed phase columns.

These hydrazone derivatives were detected by ultraviolet absorption at 360 nm and quantitated against calibration curves constructed for standard mixtures prepared from stock solutions. Other quantitative aspects of this method, including reproducibility and detection limits, have been described elsewhere (Fung and Grosjean, 1981).

Light-molecular-weight HC's (C_2 to C_6) were analyzed on-site by flame ionization gas chromatography (FID-GC) after cryogenic trapping from matrix air. Quantitative analysis involved daily calibration with a multicomponent mixture of known composition and calibration against a National Bureau of Standards (NBS) propane standard. In addition, hydroxyl radical (OH^-) concentrations in the chamber were derived from the concentration ratios of selected paraffins (e.g., n-butane:isobutane, n-butane:neopentane) in samples collected on an hourly basis. Heavier-molecular-weight HC's (C_6 to C_{12}) were analyzed by FID-GC upon return to ERT's laboratory in passivated steel canisters pressurized with matrix air. Quantitative analysis involved the use of a 38-component mixture and of a Scott-Marrin toluene standard. A number of canisters were also analyzed independently by the Washington State University method (EPA, 1980).

Two PAN analyzers built at ERT (modified electron-capture gas chromatographs with automated sampling loops) were employed for this project. The instruments were calibrated using a PAN synthesis and calibration unit also built in our laboratory. This unit consists of a photochemical flow reactor in which parts-per-billion levels of PAN are prepared by chlorine-initiated photooxidation of acetaldehyde in the presence of NO_2 in air. The portable unit allows for direct, on-site calibration of PAN analyzers in the range of concentrations relevant to ambient levels (approximately 2 to 50 ppb).

Interlaboratory Comparison of Methods for Nitrogenous Pollutants

The captive-air study experiment also provided an opportunity to carry out interlaboratory comparison studies of methods for measuring ambient levels of nitrogenous pollutants. Thus, the University of Michigan group headed by Dr. Stedman and the Unisearch Company headed by Dr. Schiff conducted measurements of NO, NO_2, and nitric acid (HNO_3) in both ambient and chamber air. The ERT staff also conducted a limited number of HNO_3 measurements, while PAN and NO_2 photolysis rate constant measurements were conducted by ERT and University of Michigan staff, respectively. Data from all three Coordinating Research Council-sponsored groups will be shared and used for modeling where applicable.

STATUS OF PROGRAM AND EXAMPLES OF PRELIMINARY DATA

The field component of this program was completed on November 13, 1981. All continuous data including NO, NO_2, O_3, PAN, individual light-molecular-weight HC's, temperature, and solar radiation intensity are being validated and processed in computerized form. Laboratory analyses of aldehydes and heavier-molecular-weight HC's have been essentially completed, as have the corresponding post-study calibrations and quality assurance tests.

Figures 7-1 and 7-2 show examples of chromatograms for light- and heavier-molecular-weight HC's, respectively, while concentrations of both light and heavier HC's for a typical sample are listed in Table 7-1. Total HC's are listed by class in Table 7-2. The most abundant paraffins in this sample included n-butane, isopentane, n-pentane, and isobutane. Toluene and xylene isomers accounted for a large fraction of the sample aromatic HC content. The substantial aromatic and low olefinic content measured for this sample were typical of the HC mix present in ambient Los Angeles air during the period studied.

Major carbonyl compounds consistently identified in morning and irradiated air samples included formaldehyde, acetaldehyde, propanal and acetone, n-butanal, and benzaldehyde. Other as yet unidentified carbonyls were often detected. Table 7-3 lists carbonyl concentrations for a typical morning air sample. It is of interest to note, in the context of the above discussion concerning the importance of initial carbonyl levels on model

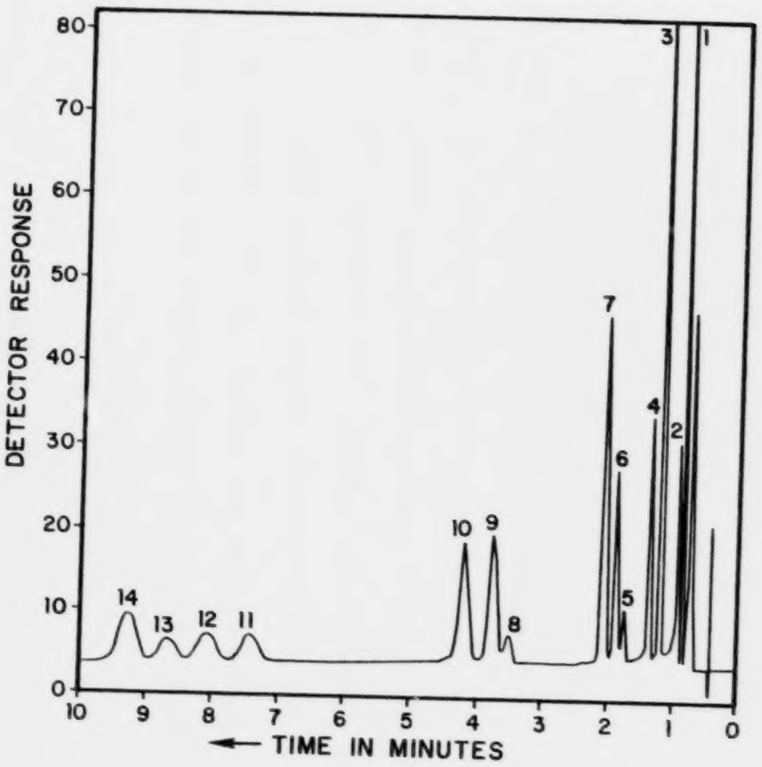

Figure 7-1. Light-molecular-weight HC's (on-site, on-line GC measurements). Peaks are identified as follows: (1) ethane; (2) ethylene; (3) propane; (4) acetylene; (5) propene; (6) isobutane; (7) n-butane; (8) 1-butene; (9) 2-methylbutane; (10) n-pentane, isobutene, and t-2 butene; (11) 1-pentene; (12) 2-methylpentane, 3-methylpentane, and methylcyclopentane; (13) cyclohexane; and (14) hexane.

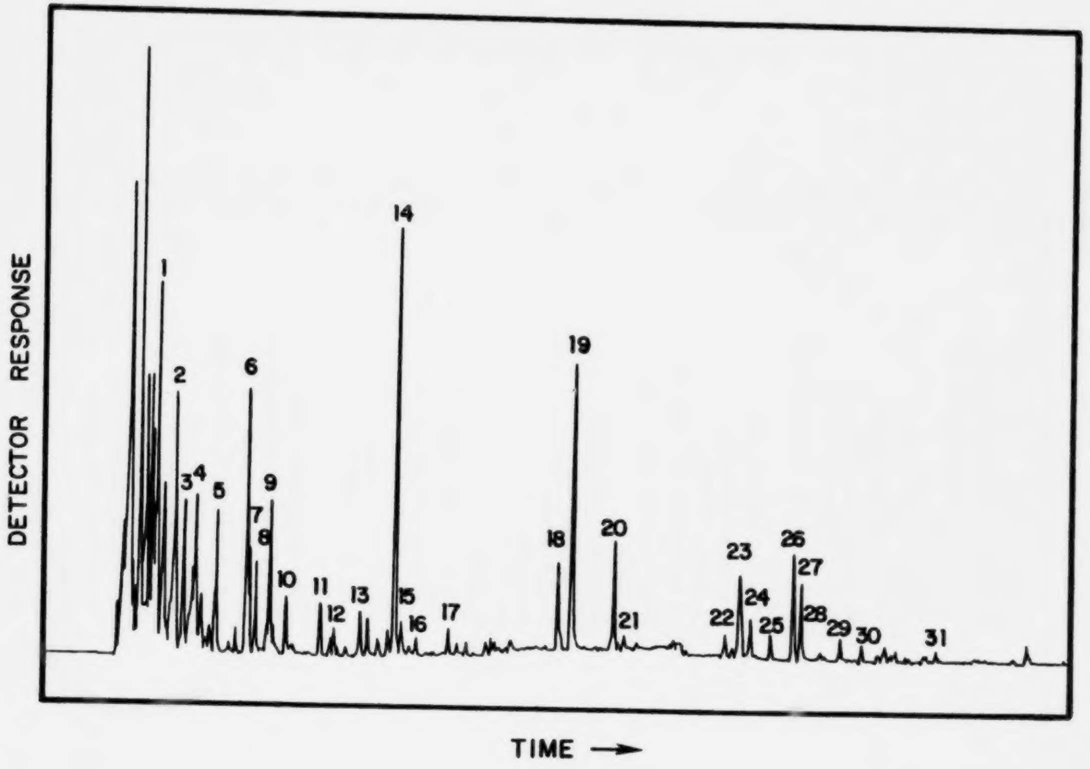

Figure 7-2. Heavier-molecular-weight HC's (FID-GC analysis of canister samples). Peaks are identified as follows: (1) 2,2-dimethylbutane; (2) 2,3-dimethylbutane and 2-methylpentane; (3) 3-methylpentane; (4) hexane; (5) 2,4-dimethylpentane and methylcyclopentane; (6) 2,3-dimethyl-2-butene; (7) benzene and cyclohexane; (8) 2,3-dimethylpentane; (9) 3-methylhexane; (10) 2,2,4-trimethylpentane; (11) heptane; (12) methylcyclohexane; (13) 2,5-dimethylhexane; (14) 2,3,4-trimethylpentane; (15) toluene; (16) 3-methylheptane; (17) 2,2,5-trimethylhexane; (18) octane; (19) ethylbenzene; (20) p- and m-xylene; (21) o-xylene; (22) nonane; (23) propylbenzene; (24) p-ethyltoluene (25) 1,3,5-trimethylbenzene (mesitylene); (26) o-ethyltoluene; (27) 1,2,4-trimethylbenzene; (28) decane; (29) secbutylbenzene; (30) 1,2,3-trimethylbenzene; (31) n-butylbenzene; and (32) undecane.

TABLE 7-1. EXAMPLE OF LIGHT- AND HEAVIER-MOLECULAR-WEIGHT HC COMPOSITION IN AMBIENT LOS ANGELES AIR

HC	Amount (μg/m^3)	HC	Amount (μg/m^3)
Ethane	13.5	3-methylhexane	7.3
Ethylene	21.8	Dimethylcyclopentanes	5.0
Acetylene	11.1	2,2,4-trimethylpentane	5.6
Propane	17.3	Heptane	5.0
Propene	10.3	Methylcyclohexane	5.4
Propyne	-	Ethylcyclopentane	-
Propadiene	-	2,5-dimethylhexane	-
Isobutane	24.2	2,4-dimethylhexane	3.1
Butane	53.2	2,3,4-trimethylpentane	2.0
1-butene	2.2	Toluene	138.7
Isobutene	6.6	2,3-dimethylhexane	0.9
trans-2-butene	5.9	2-methylheptane	4.8
cis-2-butene	-	3-methylheptane	2.7
Isopentane	48.4	2,2,5-trimethylhexane	-
Pentane	32.1	Dimethylcyclohexane	-
3-methyl-1-butene	1.8	Octane	2.7
1,3-butadiene	-	Ethylcyclohexane	1.0
1-pentene	0.9	Ethylbenzene	24.9
Isoprene	-	p- and m-xylene	109.1
trans-?-pentene	-	Styrene	1.7
cis-2-pentene	-	o-xylene	28.3
2-methyl-2-butene	-	Nonane	1.7
2,2-dimethylbutane	-	Isopropylbenzene	-
Cyclopentene	-	Propylbenzene	3.7
Cyclopentane	3.0	p-ethyltoluene	5.8
2,3-dimethylbutane	3.9	m-ethyltoluene	2.4
2-methylpentane	14.1	1,3,5-trimethylbenzene	2.7
cis-4-methyl-2-pentene	-	o-ethyltoluene	3.1
3-methylpentane	11.9	tert-butylbenzene	-
2-methyl-1-pentene	4.2	1,2,4-trimethylbenzene	9.9
Hexane	9.3	secbutylbenzene	2.2
trans-2-hexene	-	1,2,3-trimethylbenzene	1.8
2-methyl-2-pentene	-	Decane	1.6
cis-2-hexene	-	Methylstyrene	0.8
Methylcyclopentane	10.6	1,3-diethylbenzene	2.7
2,2,3-trimethylbutane	-	1,4-diethylbenzene	2.6
2,4-dimethylpentane	2.7	1,2-diethylbenzene	-
1-methylcyclopentene	-	Undecane	-
Benzene	10.4	Dodecane	-
Cyclohexane	4.6	α-pinene	-
2-methylhexane	4.7	β-pinene	-
2,3-dimethylpentane	7.3	Limonene	-
		Myrcene	-

TABLE 7-2. TOTAL HC'S BY CLASS

HC Class	Amount (μg/m^3)	Percent
Alkanes	309.6	42.7
Alkenes	53.7	7.4
Alkynes	11.1	1.5
Aromatics	350.8	48.4
Terpenes	0.0	0.0
Unidentified	27.1	

TABLE 7-3. EXAMPLE OF INITIAL CARBONYL CONCENTRATIONS IN LOS ANGELES AMBIENT AIR - 9/30/81

Carbonyl	Concentration (μg/m^3)
Formaldehyde	30
Acetaldehyde	17
Propanal and acetone	9
n-Butanal	4
Benzaldehyde	2

predictive ability, that levels of aldehydes are often comparable to those of olefins in morning Los Angeles air.

Listed in Table 7-4 are initial NO_x concentrations and the corresponding O_3 maxima for 22 irradiations conducted from September 30 to November 13, 1981 in the large Teflon chamber. During the study period, air quality in the Los Angeles area was substantially better than in previous years (e.g., the worst 1980 smog episodes were encountered in early October). Nevertheless, high initial NO_x levels were recorded on a number of days and included a high value of 660 ppb on October 6, 1981. Not surprisingly, sunlight irradiation of the corresponding ambient air sample yielded the highest O_3 maximum recorded in this project, 524 ppb.

After the results are plotted, they will be compared with the Ozone Isopleth Plotting Package (OZIPP) diagram derived from the EKMA model constructed for Los Angeles during October 1981, using the standard EKMA chemistry. In addition, an isopleth diagram will be prepared using the chemical mechanism formulated by Atkinson et al. (1981). The two isopleth plots will be compared with the experimental data to ascertain which mechanism performs better in terms of shapes of the isopleths and of control requirements to attain the NAAQS for O_3. Modeling of selected days with data obtained in the large outdoor chamber also will be carried out using the ERT chemical mechanism.

TABLE 7-4. PRELIMINARY O_3 AND NO_x DATA FOR LARGE OUTDOOR CHAMBER

Date	Initial NO_x Concentration (ppb)	Maximum O_3 Concentration (ppb)	Date	Initial NO_x Concentration (ppb)	Maximum O_3 Concentration (ppb)
09/30/81	140	136	10/29/81	150	110
10/02/81	~ 60	90	10/30/81	453	217
10/06/81	660	524	11/02/81	403	194
10/14/81	204	120	11/03/81	502	164
10/15/81	253	140	11/04/81	134	107
10/16/81	428	203	11/05/81	218	163
10/19/81	484	261	11/09/81	359	277
10/20/81	696	325	11/10/81	444	232
10/22/81	258	95	11/11/81	381	179
10/23/81	518	168	11/12/81	283	89
10/28/81	206	96	11/13/81	170	84

CONCLUSION

A protocol has been developed to evaluate the EKMA O_3 isopleth diagrams using the results from captive-air experiments. The field study for the Los Angeles experiment has been completed, and data analysis is in progress. Discussion of the possible application of the captive-air approach for assessing pollutant control measures in Los Angeles and other areas of the country should await completion of the data validation and modeling tasks.

ACKNOWLEDGMENTS

Support of the Los Angeles captive-air study by the Coordinating Research Council, CAPA-17 and CAPA-19 Project Groups, is gratefully acknowledged, as is the significant technical input provided by members of the CAPA-17 and CAPA-19 Project Groups and by Professor Jack G. Calvert in the design of this project. Mr. J. Collins, Mr. J. Harrison, and Mr. E. Breitung of ERT had major responsibility in the field operations at the USC. site, and their dedicated assistance is much appreciated.

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WORKSHOP COMMENTARY

ESCHENROEDER: I have three questions. First, what precautions did you take to prevent distortion of your alkene sample by reaction with O_3, sort of dark reactions?

LLOYD: As you notice from Table 6-4, most of the O_3 concentrations appear to be relatively low; the olefins were taken directly from the chamber into a freezing loop and then measured on site. Other samples were taken for measuring off-site.

ESCHENROEDER: That sampling time for withdrawing that sample was short enough that there wasn't sufficient time for reaction of alkenes with O_3?

LLOYD: I think that in terms of olefins, there will always be that question. We took the precautions we could in terms of trapping cryogenically and sending some of the samples away, in which case some NO was added to get rid of the O_3. I didn't focus heavily on the fact that the olefins were low in the atmospheric samples because there may be some uncertainty in those measurements because of the possible reactions with O_3 that you mention. However, for morning samples, O_3 concentrations were low.

ESCHENROEDER: You could probably estimate it from the rates, the time required, and the residence required.

LLOYD: That would be part of the data reduction. I think the major result from some of the preliminary data is that the aromatics seemed to be very high, and I think that's the major focus until we see what the olefins are for the samples.

ESCHENROEDER: What was the highest carbon number on the samples that you analyzed by chromatography?

LLOYD: I think C-11.

ESCHENROEDER: Finally, could you briefly outline how Don Stedman did his photodissociation rate measurements?

LLOYD: His standard technique was to measure the concentration of NO_2 that flows through a glass tube and then downstream measure the NO by chemiluminescence, so giving the amount of NO photolyzed.

McRAE: Have you made any comparisons of the HC composition measured against the trends of compositions you're getting out of the emissions inventory that Fred Lurmann compiled?

LLOYD: Not yet. As we saw yesterday, one thing that is lacking in most areas, and particularly in L.A., with its high photochemical oxidant, is information on HC composition. We've really got no good handle on how the character of the atmosphere may be changing. We're looking at control strategies to take effect 10 years hence.

We should make sure that our chemical mechanism can also reproduce results in those regimes that may exist in the future as well as those mixes currently existing.

McRAE: What were the typical levels of gas-phase HNO_3?

LLOYD: Those data haven't been reduced yet and I'm a little bit cautious, because we had three groups measuring the HNO_3. Grosjean is most heavily involved with that. I think from the previous Claremont study you see levels of HNO_3 up to 30 ppb. At times, again, you see levels in that range, 10, 20, or 30 ppb. These samples were taken further upwind of the USC site, and I think some of the levels in the bag are probably higher. Also, we did some measurements in ambient air, and some of those were low in HNO_3.

DIMITRIADES: Let me ask about three questions about the chromatographic analysis of the organics. First, was the identification based on retention times alone? Second, what was the fraction of the total sample you couldn't identify or that was of questionable identification? Finally, how did your HC analysis column perform? How did it perform with the oxygenates; did it result in sharp peaks or were they spread all over the background?

LLOYD: The oxygenates were reasonably resolved, although in some samples there wasn't resolution between acetone and propionaldehyde. In general the resolution is pretty good.

DIMITRIADES: I'm talking about the HC analysis column, not the MBTH (3-methyl-2-benzothiazolone hydrazone hydrochloride).

LLOYD: I'm not sure.

DIMITRIADES: The other question was what fraction of the total sample was unidentified?

LLOYD: In the example I gave here, about 95% of the sample was identified.

DIMITRIADES: Was the identification based on retention times?

LLOYD: Mostly retention times, but there was also some mass spectrometry checks for some specific compounds.

BUFALINI: My original objection to the smog chamber study was that I felt that it was doubtful that you would get meaningful results down at concentrations that would produce 0.12 ppm of O_3. The main reason for this is that I felt that chamber contamination effects would be extremely important. Could you comment on what sort of experiments were performed to make certain that the smog chamber was performing in a satisfactory fashion in the low end of the EKMA plots where one would observe 0.12 ppm? I also have another question about PBZN. I had made a calculation based on toluene that showed relatively low yields of PBZN from toluene. If one assumes about 100 ppb of toluene, which is not atypical in Los Angeles, one would observe no more than probably 1 to 2, maybe 3 ppb of PBZN; have you observed this high a concentration or have any experiments been done along that line? The yield really isn't large, and I think the experimental techniques are going to be severely tested to look for PBZN.

LLOYD: We did do some control and reference runs with propene/NO_x and butane/NO_x mixtures to check out how significant some of the dirty chamber effects would be. We haven't finished all the data reduction on that. I think that that's still of concern for some of the lesser-reactive compounds, such as the butane. Chamber contamination effects for propylene seem to be less significant, but there is no question that some effect is there, and the extent to which it's there will have to be ascertained by doing the modeling.

BUFALINI: We also found that not only chamber contamination is important, but if the bag, even a large bag, has a very small hole in it, material gets in it very readily. This is puzzling, as it would seem that most of the material would go in the opposite direction. Thus if a bag has even a slight leak in it, the results would have to be discarded. At least this is true with the 200-liter bags that we've been working with.

LLOYD: As I mentioned, we did have some data earlier than the end of September, in which we had some problems with the large chamber collapsing too early, well before the 6-h irradiation time. During the course of the experiments, leaks would occur now and again, and we would have to change the Teflon bags. Examining some of the detailed HC's as a function of time may shed some light on this effect. Regarding PBZN, again it's my understanding in talking with Dr. Grosjean that the column for PAN would have to be run for longer times, so I'm not sure that it's fully suitable for PBZN. In looking at NO_x sinks and accounting for HNO_3, PAN, and some of the organic nitrates, one might see some differences in the chromatograms which possibly may be attributed to PBZN, because I presume that they would also be reduced in the same way that PAN would be reduced and would actually give interference with the chemiluminescence instruments. After we complete our data analysis and calibration, we will know whether some of the differences we noted were real or just artifacts.

BUFALINI: It was my understanding that you had a PBZN analyzer; I think Las Vegas is using one of yours right now, isn't it?

LLOYD: There's been some talk about it, and we will probably perform PBZN measurements in the Las Vegas area in 1982.

DIMITRIADES. We would now like to hear Harvey Jeffries, who has a few things to say about work in connection with the mechanistic studies; after that, we may have some more questions on both presentations.

8. DESCRIPTION AND COMPARISON OF AVAILABLE CHEMICAL MECHANISMS

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ABSTRACT

Chemical mechanisms intended for use in air quality simulation models need to provide a reasonable compromise between chemical realism and computational efficiency. The type of approach to such a compromise can be used to define three types of mechanisms: (1) surrogate mechanisms, (2) lumped-molecule mechanisms, and (3) lumped-structure mechansims.

A list of criteria can also be defined, and how currently available mechanisms deal with these criteria is discussed. The criteria are defined from issues such as the following: the key features of smog chemistry, hydrocarbon reactivity, carbon balance, validation, useability, and documentation. In general, the performance of any currently available mechanism can be improved by updating rate constants, carefully choosing parameters, or making small modifications to the chemistry so that criteria associated with the single issue of validation can be satisfied. Therefore, the choice of mechanism should involve the entire list of issues.

INTRODUCTION

Over the past decade the scientific and engineering development of atmospheric photochemical modeling has progressed at a rapid rate. During this time the state of the art of smog modeling has advanced from its tentative academic beginnings to the point that photochemical models are today a standard tool for regulatory analysis. However, since it is neither theoretical nor experimental in the classic sense, modeling must be recognized as a relatively new area of scientific specialization. The criteria for good scientific modeling are not yet as well established as the criteria we take for granted when evaluating new theories or experiments. One area of scientific specialization apparently fostered by the expansion in modeling is the evaluation of experimental kinetics data for use by the modeling community. This presentation is, in part, intended to provide a set of criteria for evaluating whole kinetic mechanisms for use in atmospheric modeling.

Concurrent with the expansion of knowledge and modeling techniques has been a general confusion resulting from the plethora of models and kinetic mechanisms available. Clearly photochemical models are not all the same, not even in so basic a subsystem as the kinetics package. Different kinetic mechanisms give different results under similar conditions, although what "similar" means in this context is often hard to state. Each different mechanism has a different methodology for speciation of hydrocarbons (HC's), averaging of ensemble rate constants, and selection of stoichiometric parameters. Thus, if a single investigator tries to compare one mechanism againt another, he is often liable to the accusation of incorrect usage. Indeed, improper usage is likely, since few mechanisms are documented sufficiently to assure replication of results. As part of the cycle, the lack of documentation is another incentive for each investigator to develop his own mechanism. At least he will be using it "correctly."

In this review, we attempt to identify the important issues in the design of photochemical kinetic mechanisms for the atmosphere. First, we describe a general classification of mechanisms which are currently documented, and we then discuss the important features of smog chemistry as the phenomenon is presently understood. We then specifically deal with two major issues in the treatment of smog formation: HC reactivity and carbon balance. Finally, we address the issues of validation and usage of mechanisms, since these are the greatest concerns for those interested in applying photochemical models to the atmosphere.

CURRENT PHOTOCHEMICAL MECHANISMS

Photochemical kinetic mechanisms intended for atmospheric application may be classified into three types: surrogate mechanisms, lumped-molecule mechanisms, and lumped-structure mechanisms. Each mechanism differs in the nature of the simplifications it uses to make the complex reaction sequences and the multitude of organic compounds involved in urban smog more tractable.

All mechanisms tend to be the same in their explicit treatment of the basic inorganic chemistry.

Surrogate mechanisms are perhaps the easiest to understand. For laboratory smog chamber experiments involving individual HC species, mechanisms are available which treat every compound with a significant role in the chemical process explicitly. In the surrogate-mechanism approach, the explicit mechanisms for one or more HC's are added together. The complex urban mix is then assumed to be represented by some blend of the HC's treated by the explicit chemistry. The obvious difficulty with this approach is the specification of the surrogate blend. The mechanism used in the present form of the Empirical Kinetic Modeling Approach (EKMA) is such a surrogate mechanism, and a 25% propylene/75% butane mix is used to simulate automobile exhaust. The appropriate mix for nonautomotive emissions has not been established.

One possible method for adapting the surrogate-mechanism approach to HC mixes other than automobile exhaust has been offered by the users of the Lawrence Livermore grid model (known as LIRAQ). In the LIRAQ emissions inventory, each individual HC species is represented by "propylene/butane equivalents"--the amount of propylene and butane which might represent a kilogram of HC emission. This procedure has not been validated, however.

The lumped-molecule approach to kinetic modeling is the most widely used method of simplifying the smog-chemistry problem. Lumped-molecule mechanisms are based upon the approach of Hecht, Seinfeld, and Dodge (1974), wherein molecular species are classified as olefins, paraffins, aldehydes, and, usually, aromatics. The rate constant for each generalized HC class should, in theory, be an appropriate average rate of the individual compounds contained in each class. However, in practice, lumped-molecule mechanisms usually specify some default value which may or may not approximate the ensemble average.

Lumped-molecule mechanisms in general require noninteger stoichiometric parameters to describe reaction pathways for the lumped molecular species and the lumped intermediates generated by the chemistry. Choice of the proper values for the stoichiometric parameters poses a problem which is initially related to the averaging of rate constants just described; the stoichiometric parameters usually relate to the average size and distribution of the lumped initial species. However, the stoichiometric parameters in lumped-molecule mechanisms may also affect both reactivity and carbon balance. Specification of these parameters to satisfy all of these constraints simultaneously can be difficult.

The lumped-structure approach is an attempt to decouple reactivity and carbon conservation. The concept owes its inception to the work of Benson (1968), who calculated molecular reactivity from submolecular components. Thus, in the lumped-structure approach, carbon structures within the HC molecule are the lumping category. In an olefin molecule, for example, the

TABLE 8-1. AVAILABLE SMOG MECHANISMS

Mechanism	Examples	Advantages	Disadvantages
Surrogate	Dodge/EKMA (Dodge, 1977) Graedel (Graedel et al., 1975) Carter (Carter et al., 1979) AERE[*] Harwell (Derwent and Hov, 1982)	Explicit reaction scheme possible. Carbon-conservative.	Surrogate HC may not adequately represent atmospheric mix. High computational demands for explicit mechanisms.
Lumped-Molecule	Hecht, Seinfeld, and Dodge (1974) Falls and Seinfeld/CIT[†] (1978) Lloyd et al./ERT[‡] (1980) Demerjian (1979) Duewer/LIRAQ[§] (1978)	Reduced computation time. Responds to changes in HC composition directly.	Parameters difficult to specify. May change with time. May violate carbon balance. Some HC's difficult to classify, e.g., acrolein, octene.
Lumped-Strucure	Carbon Bond I, II, III (Killus, 1981; Whitten, Hogo, and Killus, 1980)	Reduced computation time. Responds to changes in HC composition directly. Carbon-conservative easy to speciate. Rate constant averaging over narrow range. Parameters can be related to explicit chemistry.	Some parameters may change with time. Treatment of intramolecular reactions can be complicated.

[*] AERE = Atomic Energy Research Establishment, Harwell, Oxforshire, England.
[†] CIT = California Institute of Technology.
[‡] ERT = Environmental Research and Technology, Inc.
[§] The LIRAQ mechanism is a condensed reaction scheme using an olefin/paraffin mixture of varying proportion as a surrogate for atmospheric HC's.

chemistry of the olefinic group is treated independently from any paraffinic side chains.

The lumped-structure approach offers several advantages over the lumped-molecular approach. Because of similar reaction rate constants, the averaging problem is minimized. Carbon conservation can be expressly maintained, and carbon balance during the simulation can even be monitored. The principal disadvantage is that intramolecular processes such as decomposition and side-chain activation can be difficult to treat. Also, because the lumped-structure approach is often less intuitive than the lumped-molecule approach, the documentation requirements may be higher.

GENERAL REMARKS ON SMOG CHEMISTRY

Ozone (O_3) formation in photochemical smog is a complex phenomenon involving the radical-initiated degradation of HC's and oxides of nitrogen (NO_x). Despite the complexity of the process, its basic features are well established, and, for the most part, noncontroversial. We will now describe some of the more basic features of smog chemistry before we analyze how different kinetic mechanisms treat these basic processes.

O_3 Generation

Ozone is the principal oxidant formed in smog. Ozone formation occurs as a result of a set of linked processes:

$$NO_2 + h\nu \rightarrow NO + O,$$

$$O + O_2 \rightarrow O_3,$$

$$O_3 + NO \rightarrow NO_2 + O_2,$$

$$RO_2 + NO \rightarrow NO_2 + RO.$$

The first three reactions above form a photochemical cycle, passing an oxygen atom from nitrogen dioxide (NO_2) to O_3 and back again. The last reaction injects oxygen atoms into the cycle. As nitric oxide (NO) is converted to NO_2, there is less and less room in the nitrogen oxide "compartment" for an odd oxygen, and the injected oxygen atoms tend to accumulate as O_3. The peroxy radicals ($R\dot{O}_2$) which inject the oxygen into the $NO/NO_2/O_3$ system are formed in the HC oxidation process.

Precursor Decay

Hydrocarbons and NO_x are the chemical precursors to photochemical smog. The oxidation of HC's yields the peroxy radicals which drive O_3 formation:

$$HC + OH \rightarrow RO_2 \ (+ H_2O).$$

Nitrogen oxides are consumed in a variety of reactions:

$$OH + NO_2 \rightarrow HNO_3,$$

$$RO\cdot + NO_2 \rightarrow RONO_2.$$

$$RO_2 + NO \rightarrow RONO_2,$$

$$\text{Olefin} + NO_3 \xrightarrow{+\,NO} \text{Dinitrates},$$

$$\text{Cresol} + NO_3 \rightarrow \text{Nitrocresol}.$$

The last two reactions are of interest because they destroy NO_x without consuming free radicals. Thus, these reactions do not inhibit the smog-formation process in the way that radical termination processes do.

Radical Sinks

Radical-sink processes are important for several reasons. Because RO_2 formation from HC is a radical-initiated oxidation process, radical sinks reduce the rate of HC oxidation and limit the O_3 formation rate.

Most radical-sink processes involve the destruction of NO_x as well. In addition to those NO_x-radical sink reactions listed above, the peroxyacetylnitrate (PAN) formation process also deserves mention.

$$RCO_3 + NO_2 \rightleftarrows PAN.$$

Peroxyacetyl nitrates can decompose thermally to yield the RCO_3 and NO_2 precursors. Thus PAN formation consumes radicals and NO_x, whereas PAN decomposition serves as a source for these species.

At high radical concentrations, generally seen only in combinations of high precursor concentrations and high HC:NO_x ratios, radical-radical reactions may become significant. The best known of these is the reaction of HO_2 with itself:

$$HO_2 + HO_2 \rightarrow O_2 + H_2O_2.$$

The product, hydrogen peroxide (H_2O_2), is an oxidant which has been observed in urban smog.

Radical Sources

To balance the effects of radical sinks and to provide a radical concentration level sufficient to catalyze the smog process, sources of radicals must be present in the system. The most important of these radical sources is the photolysis of oxygenated HC's (aldehydes, ketones, dicarbonyls, etc.), for example:

$$RCHO + h\nu \xrightarrow{O_2} RCO_3 + HO_2.$$

Another source of radicals from HC precursors comes from the olefin-O_3 reaction via several steps:

$$\text{Olefin} + O_3 \rightarrow \rightarrow \rightarrow RO_2 + HO_2.$$

Some mechanisms produce radicals from as much as 50% of all olefin-O_3 reactions. At this level olefin-O_3 chemistry becomes a significant radical source. More recent evidence suggests that the radical yield from this process is much less than 50% and that olefin-O_3 chemistry is at most a minor source of radicals.

There are two significant radical sources in the inorganic chemistry of smog:

$$HONO + h\nu \rightarrow OH + NO,$$

$$O_3 + h\nu \rightarrow (O_2)\ O^1D \xrightarrow{H_2O} OH + OH.$$

Photolysis of HONO may be significant to urban smog. Some evidence exists that this compound is emitted directly or is formed from heterogenous processes from NO_x emissions. Small concentrations (1 to 5% of ambient NO_x) have been detected in the urban atmosphere.

Radical formation from O_3 photolysis is the dominant known radical source in the rural environment, where background O_3 concentration is much higher than other sources. For urban smog this source is less important, because O_3 concentrations are suppressed in the early morning (when other radical sources are low). Later in the day, when O_3 is high, other radical sources are also high and the O1D radical source has little effect on the overall chemistry.

REACTIVITY CONSIDERATIONS

Given our basic description of smog chemistry, we may identify three factors which influence the production of O_3. The first of these factors is the radical sources needed to maintain the concentration of hydroxyl (OH) radicals necessary to initiate the HC oxidation process. The second factor is a concentration of HC's; the reaction of OH with HC's produces the peroxy radicals which inject oxygen atoms into the $NO/NO_2/O_3$ cycle. The final factor is the presence of NO_x, which react with peroxy radicals and generate O_3.

The first two of these factors, radical sources and HC oxidation, comprise what is generally referred to as "reactivity." The effects of NO_x are more complex. Although it is true that NO_x are necessary for the generation of O_3, NO_2 also serves as a principal radical sink in smog chemistry. Thus, increasing NO_x serves to reduce the radical concentration, to reduce the rate of HC oxidation, and thus to slow the production of O_3. Given a particular level of HC, increasing NO_x slows the O_3 formation rate, but increases the peak O_3 until a particular HC:NO_x ratio is reached (the "ridge line" ratio on an isopleth diagram). Additional increases in NO_x levels further slow O_3 production and reduce peak O_3, although this reduction depends greatly on factors such as total allowed reaction time, dilution rate, and heterogenous O_3 destruction.

Most current chemical kinetic mechanisms treat NO_x chemistry in a similar fashion, since the basic reactions have been studied intensively in laboratory experiments. Treatment of N_2O_5 chemistry is an area of uncertainty leading to minor differences among mechanisms. Major differences, however, exist in the treatment of HC oxidation behavior.

The oxidation reactivity of the precursor HC mix appears very similar in most current mechanisms. The principal difference in this mechanism feature occurs in the HC lumping procedure. For example, most mechanisms lump ethylene along with the other olefins, yet ethylene has an OH reaction rate constant of less than one-third that of propylene. If the propylene rate constant is nevertheless used for all olefins, the reaction chemistry of olefins may be dominated by an erroneously high value for all ethylene OH reactions. Since ethylene typically comprises 50% of olefins, the error in overall mechanism performance may be large. The effect of the error is too much reactivity early in the day and too little reactivity later in the day.

A more important difference in mechanism behavior results from assumptions concerning product yields. Subsequent to the initial reaction step, HC oxidation is dominated by the reactions of oxygenated products:

$$HC + OH \rightarrow RO_2,$$

$$RO_2 + NO \rightarrow NO_2 + RO,$$

$$RO \rightarrow HO_2 + \text{Aldehyde},$$

$$\text{Aldehyde} + OH \rightarrow R'CO_3,$$

$$R'CO_3 + NO \xrightarrow{+ O_2} NO_2 + CO_2 + RO'_2.$$

The $R'O_2$ at the end of this cycle is not the same as the initial RO_2; it contains one less carbon atom. Lumped mechanisms tend to treat all RO_2 radicals as being similar. To terminate the reaction chain, some kind of chain-length parameter is required.

Aldehydes are intensely reactive compounds. They react very rapidly with OH, and they also photolyze to generate radicals. After a period of time, the balance of aldehyde production and aldehyde loss will dominate the behavior of a chemical kinetic mechanism. Current mechanisms are sufficiently dissimilar in their treatment of aldehyde formation and loss that disparities in calculations caused by this feature will become significant in less than one day of simulation time.

CARBON BALANCE

When tested against smog chamber data, a kinetic mechanism may perform quite well. However, smog chamber experiments typically use only initial concentration of precursors, the light source may not vary in time, dilution and surface losses are fixed, and the duration of the experiment may be as short as 6 h. However, the same kinetic mechanism may not perform well for atmospheric applications which involve continuous emissions, diurnal light, complex dispersion, widely variable surface losses, and simulation times up to several days. One factor which can play a role in the quality of atmospheric modeling is the inherent carbon balance of a kinetic mechanism.

The basic function of a kinetic mechanism in an atmospheric model is to deplete the precursors chemically into intermediate products which, in turn, generate O_3 and other secondary pollutants. The rest of the model deals with generating the proper precursor levels from a combination of emissions, dispersion, and deposition, plus treating the secondary pollutants via dispersion and deposition. Hence, the improper loss or gain of carbon from a kinetic mechanism negates much of the effectiveness built into the rest of the model. The use of a kinetic mechanism validated against smog chamber data but known to have poor carbon balance adds an extra measure of uncertainty when such a mechanism is used for atmospheric modeling.

Carbon-balance analysis can be a useful tool to determine the progression of reactivity over time. To exemplify such a carbon-balance analysis, let us examine the aldehyde cycle in the Hecht, Seinfeld, and Dodge (HSD) mechanism (1974).

The aldehyde cycle in the HSD mechanism is governed by the parameter β, the control parameter for the aldehyde oxidation sequence. In the HSD mechanism, the initial HC oxidation step produces an RO_2 radical that oxidizes an NO to NO_2:

$$RO_2^{\cdot} + NO \rightarrow NO_2 + RO\cdot,$$

The lumped alkoxyl radical then decomposes to form a hydroperoxy radical and an aldehyde:

$$RO \xrightarrow{O_2} \text{Aldehyde} + HO_2,$$

The parameter β, "the fraction of aldehydes which is not formaldehyde," controls subsequent carbon oxidation:

$$\text{Aldehyde} + OH\cdot \xrightarrow{O_2} \beta\ RCO_3^{\cdot} + (1-\beta)\ [HO_2^{\cdot} + CO].$$

Subsequent reactions of RCO_3 return an aldehyde:

$$RCO_3 + NO \xrightarrow{O_2} RO_2^{\cdot} + NO_2 + CO_2,$$

$$RO_2^{\cdot} + NO \rightarrow RO^{\cdot} + NO_2,$$

$$RO^{\cdot} \rightarrow \text{Aldehyde} + HO_2^{\cdot}.$$

As long as β is less than 1.0, each of these cycles reduces the concentration of R moieties and simultaneously creates a carbon monoxide (CO) or carbon dioxide (CO_2). Several successive cycles in turn produce progressively lesser reductions in R and progressively lesser amounts of CO and CO_2, assuming no outside sources of R moiety.

Hence, the parameter β can be pictured as a ratio in the geometric series

$$L_N = \alpha\beta^{N-1},$$

whose sum (S) becomes

$$S = \frac{\alpha}{1 - \beta},$$

where N goes to infinity. The factor α represents the number of alkyl moieties (R) produced in the initial HC oxidation step (e.g., for butane in HSD $\alpha = 1$, for propylene $\alpha = 2$:

$$\text{Paraffin} + OH \rightarrow RO_2^{\cdot},$$

$$\text{Olefin} + OH \rightarrow RO_2 + RCHO.$$

The sum S, therefore, is simply the total number of whole carbon atoms of CO and CO_2 generated per original molecule. If the parameter β is chosen so that S equals the number of carbon atoms in the molecule, carbon balance is achieved. For example, Hecht, Seinfeld, and Dodge recommend a β of 0.75 for butane which gives an S of 4.0--the correct number for butane. In other words, if butane is allowed to react completely according to the pathways described above, four molecules of CO or CO_2 will be produced per molecule of butane when β is 0.75.

For HC mixtures, the setting of a carbon-conservative β is more difficult. Yet, carbon conservation is ignored if one uses β merely as an adjustable reactivity parameter or if one attempts to follow the ratio of formaldehyde to the total aldehydes. One might envision a scheme for selecting β on the basis of the average molecular weight of the mix, with perhaps some minor adjustments for the relative reactivities of the HC's involved.

We have analyzed several mechanisms for their carbon-balance properties. In most lumped-molecule mechanisms the carbon-balance properties depend upon the HC species assumed. Typically we found current mechanisms to be somewhat carbon negative for paraffins (tending to lose carbon faster than an explicit mechanism), whereas carbon balance for olefins tended to be somewhat carbon positive (yielding more carbon in the products than exists in the precursors).

One mechanism that we examined was actually carbon divergent, each aldehyde cycle yielding 17% more aldehydes than the previous cycle. Under some conditions such a mechanism would yield highly nonphysical results.

VALIDATION OF MECHANISMS

The problem of model validation is not confined to photochemical kinetic mechanisms or even simulation models in general. The problem of hypothesis testing is central to the scientific endeavor. No rigorous procedure which guarantees a validated simulation model is presently available. We will, however, attempt to describe certain criteria which, if met, will support the belief that the mechanism in question is a reasonable description of the underlying physiochemical processes.

Chemical Foundations of Kinetic Mechanisms

Because of the assumptions and extrapolations which must be made in applications of kinetic models, the fundamental basis for these models should be sound and robust. The central chemical reactions and reaction rate constants used in the mechanism should be the most accurate available; where uncertainty exists, the limits of that uncertainty should not be exceeded. The mechanism should also conserve mass and avoid the use of arbitrary tuning parameters whenever possible.

However, a mechanism which violates one of these rules is not necessarily invalid. Since some uncertainty still exists in the rates and products of the important chemical reactions in smog formation, we may consider all kinetic mechanisms to be in error to some degree. However, the behavior of smog chemistry is insensitive to changes in some reaction rates. In many cases it is the ratio of competing reactions that determines overall behavior; if the ratio is correct, the mechanism is valid even though the absolute value of the rate constants may be incorrect. Even violations in mass conservation may have an insignificant effect under many circumstances.

The essential point remains, though, that a mechanism which exhibits fundamental chemical realism is more valid than a mechanism which does not. An explicit mechanism is, therefore, fundamentally more robust for the specific HC's for which it was developed. This point provides a methodology for testing lumped mechanisms--they should be comparable to explicit mechanisms.

As we have previously noted, all current mechanisms tend to treat inorganic chemistry similarly. Inorganic smog chemistry is well characterized by direct kinetic measurements--the first validation of any photochemical mechanism. The organic chemistry of some organic molecules is also well characterized. The ability of a lumped mechanism to simulate the known chemistry of these organic molecules (as reflected in an explicit mechanism) forms the second validation test of a lumped mechanism. Note especially that in comparisons between mechanisms, one is not limited to comparison with observed species; one may compare predictions using computer output from explicit mechanisms for short-lived intermediates, for example, OH and $RO_2\cdot$, as a further validation check. The greater the degree of correspondence for all species between the lumped and explicit mechanisms, the more stringent the validation test and the more sound the construction of the lumped mechanism. This last point (the use of all species) is also applicable to the validation of mechanisms using smog chamber data.

Validation Using Smog Chamber Data

The use of smog chamber data is indispensable for the development and validation of chemical kinetic mechanisms. In our own efforts to simulate smog chamber experiments, we have developed a number of methodologies for the improvement of the validation process. These include the following principles:

- All modeling exercises should attempt to simulate not only the O_3-formation behavior of the smog mixture, but also NO_x, HC, aldehyde, and CO data, within the limits of experimental uncertainty.
- The experiments used as a validation test of a lumped mechanism should include a broad spectrum of reactivity. Experiments at different precursor concentration levels and different HC:NO_x ratios should also be performed.
- For lumped mechanisms, validation using a variety of HC mixes should be attempted even if their reactivity is known to be similar. This should certainly include "realistic" mixes such as auto exhaust.

- If possible, some experiments should be run to completion, that is, to a point where either HC or NO_x are depleted so that a true O_3 peak is reached. In an outdoor chamber this may require a 2-day run if the diurnal change in sunlight produces the O_3 peak.

The issue of chamber-related effects is controversial, but several points may be made. First, the successful application of a mechanism to several different chambers certainly enhances claims for its validity. Second, some chamber effects are fairly well characterized and thus do not necessarily detract from the validation of a mechanism. The surface loss of O_3 may be such a chamber-dependent effect; the shape of the light intensity spectrum can be another chamber effect.

The use of "adjustable" chamber effects in the development of a mechanism can obscure the fundamental photochemical process and limit the area of its validity. For example, the use of large, chamber-dependent radical sources in the application of a mechanism to a smog chamber obscures the validation of that mechanism with regard to radical source and sink phenomena.

Our own work has involved the study of numerous kinetic mechanisms validated for several different smog chambers. We believe that smog chamber effects are such that validation of mechanisms is entirely possible at urban-level precursor concentrations. At lower concentrations of HC and NO_x ($<$ 0.2 ppmC HC and $<$ 0.05 ppm NO_x), chamber contamination becomes a problem for many facilities, and special methodologies must be used if the smog process is to be studied under these circumstances.

An analogy between electrical circuits and smog chemistry can be used to help explain the sizeable O_3 concentrations seen from smog chambers when no precursors are added. The flux of radicals is comparable to the current of electricity and O_3 comparable to the voltage or the signal generated. Thus high-concentration experiments have the robustness of a low-impedance circuit and low-concentration experiments are subject to spurious effects even though the O_3 or signal strengths of the two types of experiments may be similar.

MECHANISM USAGE

The application of photochemical kinetic mechanisms to atmospheric simulations places another set of criteria on mechanism comparison. Ideally, a mechanism intended for atmospheric applications should be computationally compact, and straightforward methodologies should exist both for the speciation of emissions into the generalized species and for the selection of parameters such as stoichiometric coefficients and photolysis rates. Finally, if the mechanism is ever to gain general usage, it must be well documented.

Computational compactness is a prime requirement for mechanisms used in models that include an adequate treatment of atmospheric transport processes. Such models often reduce the computational overhead by invoking the steady-state approximation for many of the intermediate chemical species of the mechanism. To make optimal use of this approximation, the mechanism should be designed with a minimum of non-steady-state species. Furthermore, reactions between steady-state species must be held to a minimum, since such reactions increase the algebraic complexity of the steady-state equations.

Converting a complex mixture of HC's into the special precursor species of a given mechanism is often the most difficult task confronting the user of a kinetic mechanism. Although it is relatively easy to specify the HC categories for simple olefinic or paraffinic compounds, more complicated compounds defy such easy analysis. Acrolein, for example, has both an olefinic and an aldehyde functional group. It thus cannot be placed easily into a lumped-molecule mechanism. Such concerns were an important factor in the development of the lumped-structure approach. In the Carbon Bond mechanism, for example, acrolein can be treated as one olefinic group and one carbonyl group. Another type of example is octene. Most of this molecule is paraffinic, yet it is technically an olefin. A surrogate-mechanism approach might consider octene as a blend of propylene and butane; a lumped-molecule mechanism could do likewise or treat octene as a pure olefin precursor making special adjustments to the intermediate parameters; a lumped-structure mechanism merely treats octene as six paraffinic units and one olefinic unit. If octene is treated as a pure olefin using a lumped-molecule mechanism, then the parameter adjustment must also be appropriate to the overall mixture. Noteworthy is that the concentration of the special olefinic species would typically be the same in all three types of mechanism for this example.

One feature that is useful in a kinetic mechanism is comparability with normally observed concentration data. Both surrogate mechanisms and lumped-structure mechanisms can be compared to total nonmethane hydrocarbon (TNMHC) measurements. Such a comparison is more difficult for lumped-molecule mechanisms because chemical reaction tends to alter the average molecular weights of the HC mix. Similarly, mass-balance calculations during a simulation are difficult for lumped-molecule mechanisms, but are simple for surrogate and lumped-structure mechanisms.

If a mechanism is sufficiently detailed to warrant it, certain individual HC's may be treated explicitly, while those remaining might still be fitted into the lumped-species concept. Two possible candidates are ethylene and toluene. Both are significant contributors to ambient HC mixes; each has been observed to constitute as much as 10% of the total reactive mix. Each is sufficiently different in reactivity from related compounds to warrant separate treatment. Each has an OH reaction rate constant that differs from similar compounds by a factor of three. Separate treatment of these HC's may then allow comparisons of model predictions to observed data for the purpose of source reconciliation and a unique check on the combined model performance from emissions, chemistry, and dispersion.

Related to the speciation problem is the problem of lumped-parameter estimation. Attempts to design mechanisms around this problem run into conflicting goals. The greater the degree of lumping, the more difficult and important the parameter estimation problem becomes. Yet lumping is required to reduce computational requirements. As we have already seen, the lumped-molecule mechanisms often present difficulties arising from a conflict between reactivity and carbon conservation. This tends to happen whenever a parameter is used for two purposes. Generally, therefore, a parameter should not have multiple effects; but again, the greater the degree of lumping in the system, the more difficult this task becomes.

Documentation

As a general rule, a flexible mechanism requires extra documentation to implement that flexibility. The purposes of documentation are several:

- To describe the theoretical basis for the mechanism, and to demonstrate its consistency with current knowledge.
- To document its validation for smog chamber experiments.
- To describe the methodologies for its use in applications.

A useful part of such a document would be a set of default parameters for use in those circumstances wherein the detailed knowledge required to determine such factors rigorously is lacking.

The ultimate test of a mechanism's documentation is fairly simple. An inadequately documented mechanism is rarely used by anyone, save its developers, even though the mechanism has been judged by many reviewers to be the best available.

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WORKSHOP COMMENTARY

DERWENT: I like your separation of the reactions into what they are actually doing. I'd like to ask if you have considered putting a further class on the end of your reactions, which consists of those reactions describing the behavior of the secondary conclusions.

You've talked about O_3 generation. What about discussing those reactions that lead to O_3 loss? These might include deposition, but they might also include reactions with HO_2 radicals or something like that. Also, you might discuss the processes that lead to the loss of PAN and aldehydes, because they may be treated quite differently by the various reaction mechanisms you're covering.

WHITTEN: Yes, that is true, though I didn't go into it. I did mention the idea of aldehyde balance over a period of time, but I didn't really emphasize any idea of performance because I think that is Dr. Jeffries' main area, which he will be talking about today.

A mechanism certainly must be able to follow the generation of O_3 and the O_3 concentrations that are seen. That includes having proper source and sink reactions of O_3. Certainly the cycle I showed was the basic, simplistic, single main area of O_3 generation. Reactions of HO_2 and OH with O_3 are surely well known and need to be accounted for.

I might mention, also, that a significant side issue to having a proper aldehyde balance, radical source balance, and sink balance is that when you end up having the right OH concentrations, you get the right HC decay.

All of those things are important criteria to look for before you look at how well it fits O_3. For instance, you may have an O_3 mechanism that, when you put material in a smog chamber, starts with the same amount of material and makes the same amount of O_3, but the HC's don't decay at all or they decay too far. When used in the atmosphere with continuous emissions, e.g., in a 2-day situation, you would be doubtful that this mechanism would really perform over a wide spectrum, even though its performance in that initial test was really quite good. So, I think that HC decay, precursor decay, and aldehyde balance are all involved and are connected to maintaining these radical sources and sinks that are secondary to precursors.

DERWENT: Secondary products decay as well.

WHITTEN: Right. Like PAN, for instance. It forms and decomposes and if there is NO around it reacts with it. Actually, the radical that is formed reacts with NO, and then you don't get the PAN back. It is very sensitive to that.

McRAE: Dr. Whitten, in your talk you emphasize the importance of carbon balance. Could you give me some indication of how much uncertainty, on a typical day, the O_3 production would generate using one of these mechanisms?

WHITTEN: Well, you can put together a hypothetical experiment with a mechanism; just say put a pure aldehyde--

McRAE: I mean for the typical values of the different mechanisms that you mentioned.

WHITTEN: I'm not quite sure what you're trying to get at, because it's difficult to define what's typical, and then say what's typically important. I think the point I was trying to make is that there should be something involved in the choice of the mechanism concerning how it deals with this particular problem of carbon balance.

The molecular-species-type generic mechanisms deal with this through the parameters that they have. I pointed that out generally.

KILLUS: What becomes important in a single day's reaction, in urban application, is what the level of aldehydes is that you reach given a certain input of HC's, that is, what the equilibrium level of aldehydes is that you reach. That tells you what the reactivity of the mixture is.

In a mechanism which does not lose aldehydes fast enough, for example, or one that loses them too rapidly, that level becomes very different, even in the course of a day. From our experience operating the Carbon Bond mechanism for both the urban mixes and the theoretical type simulations, the usual level may be perhaps 20 to 25% aldehyde in total carbon balance within a relatively short period of time. By a short period of time I mean, say, 2:00 or 3:00 p.m. in Los Angeles, that is, by the time you get out near the Riverside area.

For a mechanism that in some extreme cases does not lose aldehydes at all, or in the most extreme case, one that actually gains aldehydes during that time, that 25% level becomes unbounded. In the case of a mechanism that doesn't lose aldehydes obviously you lose HC's if the aldehydes remain there, and so eventually you get entirely 100% aldehyde/smog mixture and no HC precursors whatsoever.

That would probably take maybe 3 or 4 days, as near as I can tell from general HC decay. But, you exceed the 20 to 25% level within the course of a day.

LLOYD: Dr. Whitten, you mentioned carbon bonds and I think also NO_x bonds. I think the Carbon Bond mechanism has been an excellent approach for giving good fidelity to the chemistry going on and yet making the package usable in an urban airshed model. However, as you mentioned, we are not faced with those same constraints for EKMA. I think we already have some mechanisms which separate out ethylene, toluene, etc. Thus, I would like to hear your comments on how far you think we can go with looking at more explicit chemistry which can be used in EKMA, consistent with what we know about the atmosphere.

Do you have any comments on that?

WHITTEN: We have done some EKMA modeling where we split specific compounds out of the carbon-bond chemistry and looked at those separately for specific contrasts.

Recently, we looked at eye irritation from toluene in the Las Vegas area. The reaction is propelled by chlorine. We had the carbon-bond chemistry to take care of the regular HC stuff and another separate chlorine package associated with it.

I think this is done quite regularly, and it's something that I would recommend, that in future versions of EKMA there be some expanded amount of chemistry. Especially since the chemistry package in EKMA seems to work rather efficiently and is not very limited, having to have a highly condensed mechanism. It's not like the air shed model, so I think your point is very well taken. It has been used, and I support it very strongly.

In terms of what you said about NO_x balance, I tried to point out that the NO_x chemistry, by and large, comes from the evaluation studies that have been made in stratospheric chemistry. There is really only a NO_x decay associated with smog chemistry. There is no NO_x formation like you get in the stratosphere from nitrogen molecules. So, the balance is one of nitrogen decay, which I did discuss as being an important factor.

The carbon balance is a different story because of the possibility that it would make carbon or decay carbon. You can make it within parameters. There are no parameters that are associted with the NO_x chemistry. That is explicit. So, there is not really a problem with nitrogen balance because of the lack of parameters.

LLOYD: When you were talking about the simulations in Los Angeles particularly, I heard you say and I heard Dr. Killus say on a couple of occasions, "what's right." How do you define "what's right" when you're talking about model simulations? What have you got to compare it with?

WHITTEN: That's certainly a good question. When I say "what's right," it means I have some 2-day information, both in terms of what characterizes the age, the aldehydes, and the total mix in the atmosphere. We also have some--

LLOYD: You had the ground-level measurements and didn't have the elevated levels?

WHITTEN: I believe that's true, although I believe there may have been some--I'll have to check on this--I believe there were some at elevated levels.

WHITTEN: Certainly, in smog chambers with certain mixes, one could track these species fairly well. There are even some fairly long-term smog chamber data; for example, Dr. Jeffries observed more or less what's going on.

More importantly, we compare the aldehyde buildup to explicit mechanisms; that is, if you look at an explicit mechanism and observe where the aldehyde concentrations develop, those should be matched by a lumped mechanism. This explicit mechanism would have all the chemistry, as best we understand it.

Now, if there are errors in the explicit chemistry, certainly there will be errors in the chemistry derived from it.

I daresay that such derived chemistry is more right than chemistry which disagrees with the explicit chemistry as we know it. Certainly, though, in situations where your aldehydes don't go away, it's wrong. So we do have some bounds on it. If the mechanism ever exceeds those bounds, we know, of course, we've made a mistake.

WHITTEN: I might add that the radical balance in mechanisms is currently not always handled the same.

Ken Demerjian's mechanism obtained some of its radicals from the O_3 olefins, more so than other mechanisms, and therefore it behaves differently for generated O_3. Dr. Jeffries will show that it produces difffernt shaped curves. We feel that such differences in the shape of the curves are associated with response to the aldehyde balances. There is uncertainty in the yield of radicals from the O_3 olefins.

LLOYD: Do you feel that there are sufficient smog chamber data available for mechanism testing, or would you like to see more data?

WHITTEN: I'm not going to say that more total data are needed, but I will say--

JEFFRIES: There are never enough.

WHITTEN: Right, there are never enough good data. But there is a tremendous volume of data. We have computer tapes and tapes of data from about 20 smog chambers. In fact, we don't have time to look at all the points on alm 1,000 runs.

I think there should be a test set put together. A set of smog chamber runs should be used to look at any potential candidate kinetic mechanism, if you're going to use a model like EKMA, that gives us sufficient reproduction of this set of smog chamber runs.

If the mechanism qualifies at that level, you'd want to use it. If the mechanism can't reproduce that, without assuming some unbelievable chamber effects or something like that--

DODGE: What set of data would you recommend?

WHITTEN: Well, I think one could use the current Bureau of Mines data, or the set of data that was put together at the University at Riverside where they looked at a range of reactivities of high aromatics and low aromatics.

Also, I think Dr. Jeffries has put together a set of experiments that could be used. One could have some automobile-exhaust experiments, some fixed light-evacuable-chamber-type experiments, and some field experiments. I think this set should probably include a 2-day experiment like the one that Dr. Jeffries is working on.

It shouldn't all be in one chamber. It shouldn't all be the same type of thing; there should be some spectrum involved there.

WHITTEN: I think you run the risk of some bias in a set by just saying that data from this one chamber, this one set of data, is the only one. I think you need to look at the spectrum of data.

JEFFRIES: The issue here is not that a set of smog chamber data represents the truth; it's that a set of conditions for which we have some experimental information represents a good basis for all the mechanisms being compared against each other as well as against the smog chamber data. This is what you find when you do that, this mechanism does perform in some way relative to all other mechanisms you go through and also relative to this whole wide range of data.

It's very clear that one chamber is not adequate for that purpose, nor is the kind of experiment typically run in a smog chamber satisfactory for models that are going to be used in the ambient environment.

McKEE: Did I understand you correctly? Are you suggesting that to obtain the data for this kind of modeling technique, emissions inventories should be compiled in terms of molecular-weight range of the olefins present and the aromatics and so on, and that once you do all this you would monitor, presumably continuous ethylene or toluene or some one constitutent as a surrogate, for this whole mix in the emissions inventory. Is that the approach you're talking about here, Dr. Whitten?

WHITTEN: The approach that I was talking about is a little bit like that, the idea being that all of these mechanisms have some condensation involved in them. You lose sight of how well the HC decay is doing and how well your overall model is going in terms of emissions.

Carbon monoxide is sometimes used for that, but it doesn't really test the kinetics very much. Unless your emissions inventory and meteorology for CO levels aren't close to what's being measured, you have a feeling that something's wrong with your meteorology, your model, or your emissions inventory. But there is really nothing like that now in HC's. We have no tests on emissions inventory. We don't test the dispersion quality of a model or how the chemistry is doing in the atmosphere.

McKEE: Well, two things about this occur to me. First, the data requirements for compiling that type of emissions inventory appear to me to be several orders of magnitude above what is affordable. I am told that many companies in the Houston Ship Channel area now are spending over $100,000 a year for engineering time just to maintain the basic data that go into periodic emissions inventories which are measured in total hydrocarbons (THC's) without any breakdown.

If you have to give this kind of a breakdown, it seems to me that the costs would be more like $100 million instead of $100,000, or some--

WHITTEN: I didn't mean to imply that it had to be done everywhere with equal vigor. What I meant was that it might be possible to test some of the models or mechanisms that are currently available with atmospheric tests.

Some areas of the country have very detailed emissions. We heard about gas chromatographic (GC) measurements of what's in the atmosphere a few minutes ago.

The Air Resources Board in California has broken source categories down into about 200 different specific molecules. And each source category--

McKEE: Do all large refineries and petrochemical plants submit an emissions inventory broken down in these terms?

WHITTEN: The individual pounds and the individual molecules; very, very detailed.

McKEE: Are those updated every hour or every day or every time a unit malfunctions or a compressor's lost, or something like that?

Composition will change radically and O_3 formation will react to that change, we think, on the basis of an hour or two if there is a major malfunction in one large unit.

This brings me to my second point. Your ethylene monitoring will not give a surrogate for that whole mixture because if a billion-pound-a-year ethylene plant loses its product compressor, the ethylene concentration in the air at your monitoring station 3 to 4 mi downwind might suddenly go to 10 or 20 times what it was before, but the other HC constituents in the atmosphere may not have changed very much. So, I don't see ethylene or any other one component being a surrogate for your whole emissions inventory on a short-term basis.

WHITTEN: I think it wouldn't be on a short-term basis, and I think that if all of this were to be done and it didn't work, you'd have to come up with this sort of explanation. However, I think that not doing it, even though the information in some cases may be available, is perhaps forfeiting an opportunity to test models in a way that they are not being tested.

McKEE: Theoretically I agree with you, but as a practical matter I don't see that kind of information being available. The proportion of the molecular weight range of olefins and aromatics and other constituents is going to change every time a plant gets in a crude oil supply from a different supplier. They are scrambling for crude oil all over the world and are getting all sorts of different crude from time to time. Every tanker that comes in is different, in some cases.

Secondly, every time there is a malfunction or process upset or a change in catalyst activity, or something like that, the molecular composition of the emissions from that unit may change rather drastically over a period of a few hours or a day or two. I don't see how all of this can be kept catalogued and updated.

WHITTEN: I'm not suggesting that, by any means. I'm suggesting that it be used where the information is already available, for instance, in the Los Angeles area. In Los Angeles they do source categories and break down average emissions into the number of pounds of each particular kind of molecule that is coming out.

This all gets blended together over a large area, and a lot of these fluctuations tend to average out. If you get an average concentration of ethylene and of toluene, which can be monitored, you can look at a lot of the things Alan Lloyd suggested where we can see toluene every day and aromatics coming up at between 25 and 30% every day. Then you can have a model that has 20% toluene in it, treated separately.

I think these fluctuations in the Los Angeles Basin aren't necessarily seen, and that would be a short-term model.

If you wanted to put together a model that would tell what really happens to smog in Houston when there's an upset in an ethylene plant, that's a different thing. You would look at that individual plume and study it and put an upset in your model. That's different from modeling a whole smog problem in a city where things are mixed together more and all of these fluctuations have averaged out.

MEYER: Trying to reconcile some of the practical concerns that have been expressed with the desirability of monitoring certain species, I'm wondering if it would be useful to do a chromatographic sum of species and monitor the diurnal patterns of those kinds of readings. You could then test that against the mechanism?

WHITTEN: I don't know whether or not it's necessary to do that in every city over a long period of time, but, I do think it would be helpful to do it in one or two places. We need to get out and use the models to find out what's wrong with them.

It would have to be in terms of checking out the models that are in use. Once you have decided that the model works great, you don't need to worry about those little details. I don't think you really can say over a long period of time that every city in the country would have to have this much.

DIMITRIADES: Can we get around the problem Dr. McKee mentioned by doing ambient analyses, rather than by offering some composition of the emissions? Perhaps we could get the composition information by analysis of ambient data in the morning or at some time when--

MEYER: Is it the composition that is that important or is it the decay of the total mix?

WHITTEN: For a model to work properly, if it's a good model and can adjust to that, it will show what the composition is, whether it's in emissions inventory or validated through the monitoring data. But, to see if a chemical mechanism really works over a long period of time, it has to be tested during the day when the models are really working in the atmosphere.

I think atmospheric testing of these mechanisms and models is important. We need to have more tests to give us more confidence that they really are working and can be used more. This is one piece of data which helps check out the combination of the model all working together. It's a check on the model.

KILLUS: I saw an emissions inventory from the Houston area just last week. I believe it was prepared before that. It said that the fraction of aromatic HC's in the Houston area was 4%.

I've seen also a significant amount of GC data from ambient Houston air. It indicates that the concentration for the proportion of toluene in the Houston area is at least 5% and more likely 10%.

Given these two pieces of information, which is a very small amount of information, one conclusion is that the emissions inventory was incorrect and should have been redone in some fashion. However, going to every single emitter and having them prepare hourly estimates of what their fractionation is is probably not necessary. It certainly is necessary to do it at a greater level of detail than what was done for the emissions inventory project that I saw.

McKEE: Whether it's necessary or not, it's impossible.

KILLUS: I don't think it is impossible to do on a yearly or bi-yearly basis in a general fashion. We'd then have it to compare to GC analyses. They certainly do it in Los Angeles, and it doesn't seem to have bankrupted the city. I see no reason why something similar to that couldn't be done in the Houston area.

MARTINEZ: It is clear that the models are going in the direction of greater fidelity in the way of reproduction not only of the O_3 but of the HC's, also. At some point, the models and the inventories have to be married. If there is a total unwillingness to come up with inventories that are appropriate for the models, then you have to make it efficient; junk the models, or bite the bullet. It's being done in California and probably will be done elsewhere, too.

WALKER: In response to your comment on Houston, the enormous effect of the micrometeorology on the location of emissions at any one point is so large that unless you had a very well located set of many, many samples taken, I would think you would have very little chance of ever having an emissions inventory check of some random samples of the atmosphere. Most of the samplings I am aware of that have been taken in Houston have been taken at sites predominantly influenced by automobile and vehicle emissions. Contrarily, I would suspect the emissions inventory you saw was largely industrial emissions. It probably did not even have the area sources added in.

KILLUS: At least one of the GC data sets I saw came from the Houston Ship Channel itself. I don't believe that that's an area dominated by automobile emissions influence.

WALKER: And that was 5%--

KILLUS: That area showed, in fact, 20% aromatic contribution.

WALKER: It could have been 2 km downwind from a BTX unit. That certainly doesn't make that a typical sample of the whole area.

KILLUS: I also know that that particular emissions inventory was prepared by going into the volatile organic compound (VOC) manual and getting four individual random-source profiles and applying them to the generic area in Houston. For example, they used a commercial site and an industrial site, not even bothering to use a chemical-industrial site. It was quite clear that the emissions inventory was inappropriate.

WALKER: I agree. But I agree with Dr. McKee also. I don't think you can get them much better very easily.

CARTER: I have a couple of comments, first related to what they were talking about. No matter how difficult it is, we need to have some idea of what the HC composition is, just so we can know how to test the representative chemical models.

Also, you were discussing the validity of smog chamber data and their performance. One point I don't think was made strongly enough was that for a model to be valid, it has to not only fit smog chamber data, but also, its parts have to be consistent with basic laboratory studies, such as kinetic studies. If it isn't, how can it have any validity? It may just fit, but that could be simply partly coincidental.

Our knowledge of the chemistry has come to the point that we no longer have to rely on engineering approaches, at least to smog chambers. We know most of the major reactions and at least the magnitude of the major smog chamber effect. So we really can fit the simpler alkanes, olefins, and aromatics to the smog chamber data without arbitrary adjusting of parameters. But, even if there is disagreement about whether adjustment of parameters is arbitrary, at least the known part of it should be consistent with basic results.

The one problem I have with some of the discussion, especially of the EPA model and the chemical mechanism that's in the Ozone Isopleth Plotting Package (OZIPP) computer programs that I saw, is that a number of the individual rate constants and mechanisms are just plain wrong, based on our current knowledge of the chemistry. Some of them have the wrong HO_2 plus NO rate constant, the wrong OH plus NO_2 rate constant, or the wrong OH plus propylene rate constant, and yet they're still being used.

An incorrect mechanism may fit smog chamber data, but so would something perfectly arbitrary, like using those five parameters you're talking about with the EKMA models. That would be a more honest and straightforward approach than using an incorrect mechanism.

Concerning the reactivity of compounds, one other type of reactivity was being considered, and I'm sure you will agree that some types of compounds act as radical inhibitors in their mechanism. In particular, we have evidence that the larger alkenes in their mechanism have a considerable amount of termination involved, and if you have a termination of radical levels, it's opposite the way aromatics behave. That is another aspect of reactivity that needs to be considered. As you know, I don't agree with your conclusions about radical sources, so I'll be discussing that today.

WHITTEN: I certainly agree overwhelmingly with your comments. First of all, I did a very poor job of emphasizing the importance of what I meant to talk more about, actually the foundation validation part. I had intended to say more, I just forgot. Thank you for pointing that out.

The mechanism is built on a strong foundation of pieces which are individually checked out. We have, for instance, the inorganic chemistry which has been recommended by a group of eminent scientists working in that area, and you have the formaldehyde which is basic to absolutely every form of smog. So, you can do a smog chamber experiment with just formaldehyde, and test that NO_x chemistry and the formaldehyde.

Any modern mechanism should be able to do that; it should have the formaldehyde chemistry built into it. I think they do. If you have higher aldehydes and other forms of chemistry or just propylene, it should work for just propylene.

On the other hand, there is another problem. Perhaps some generic mechanisms actually perform better as you go to a more complex mixture. I think that when looking at a pure compound, you may have to adjust the mechanism to account for the fact that it's a pure compound and not a mixture.

Some mechanisms have been developed really to deal with a mixture effect. Dr. Jeffries has studied some of these effects in his recent smog chamber experiments.

As you blend these mixtures together, you get some strange effects. When things start to disappear there's a leveling effect.

CARTER: I understand the curves. For EKMA models, at least, you can get the detail that you want. Wouldn't it be better to start with a more detailed model instead of adjusting the mechanism or adjusting the representation of the mixture using six or eight different HC's and aldehydes? If you know what the mixture is in the ambient air, especially--

WHITTEN: As Dr. Dimitriades said yesterday, there are things that have a positive and a negative aspect. When you use a mechanism that accounts for a wider spectrum of compounds than propylene and butane, instead of an explicit mechanism for propylene and butane, you may be sacrificing the carbon-balance effect that this mechanism has. It's a nice clean mechanism for propylene and butane.

You put your problem in a different place; the emissions inventory or the reactivities. But, once you've decided that a certain ratio of propylene and butane actually represents how a mixture reacts in the atmosphere, your model now is carbon conservative. Your model, within itself, is not going to have problems. You don't have to worry about it.

JEFFRIES: Are you suggesting a mechanism with 20 or 30 explicit pieces?

CARTER: I don't think it's necessary to have that many, because it's--

JEFFRIES: Well, 5, 10?

CARTER: Actually, I was able to fit the surrogate smog chamber data with just three: propene, butane, and formaldehyde. Perhaps for something with more aromatics I would have to add an aromatic and different classes of things, but there aren't 30 different ways that things react.

JEFFRIES: How do they differ from a regular lumped mechanism with, say, two different kinds of olefins, two different kinds of aromatics, or three different kinds of aldehydes?

CARTER: Well, if the details are chemically reasonable and it doesn't have reactions that have no basis in reality, and the mechanism is sufficiently flexible--

DIMITRIADES: The comment I want to make is that I think I have an answer to your remarks, Dr. Carter. The EKMA mechanism uses all kinds of inaccurate data. There is a good reason for that, but it is involved and needs to be explained. to raise this question in the afternoon general discussion when we can allow sufficient time. But, for the time being, I would like to ask Dr. Whitten a question.

You suggested two methods for validating a mechanism; one is based on explicit chemistry and the other on how well the mechanism fits the smog chamber data. You didn't say anything about a method based on how well the mechanism fits ambient data. Am I to take it to mean you don't think very much about a method based on ambient data?

WHITTEN: I touched on that issue by talking in our discussion about having toluene broken out. I'm in favor of it, but once you get out into the atmosphere, you have the problems of emissions and dispersion. You need some way of knowing that emissions and dispersion are okay, so that you can say if the mechanism works, the model works, and it's the chemistry that makes it work. Or if it doesn't work, it's the chemistry. I think at the moment there is uncertainty.

If you don't have the correct meteorology in the model, the correct emissions, then whether the mechanism works or not, you don't really know. If the model seems to work, it could be a combination of compensating errors, and if it doesn't, it could be because -- that's a problem you don't have in the environment of the smog chamber as long as you have your impedance low enough.

ESCHENROEDER: But you get yourself into a logical trap, because you're going to use the model in that messy environment, ultimately, and take it seriously. So at some point I agree with Dr. Dimitriades. You have to face up to these imperfections that you don't have in the laboratory-controlled study.

DIMITRIADES: When you deal with ambient data, you have meteorological factors and chemical factors all compounded together. Can you delineate all those effects so that you will be able to concentrate on, say, validating this one aspect of the model, the chemistry?

Is this feasible? Everybody agrees it's desirable. But can we do it? Is it possible to use atmospheric data for the purpose of validating the chemical mechanism, that is, isolating just that aspect of the model?

WHITTEN: I think we're getting pretty close in that we have some pretty detailed emissions inventories in Los Angeles; we have some detailed compositional results for Los Angeles and we can follow the composition, the percentage of aldehydes, and some specific compounds throughout the day.

There may very well be a set of LARPP data, or a set of Los Angeles data for which you could say, this is part of the validation test, this and the smog chamber data. Then you ought to be able to test this trajectory that has been worked over for hours and hours and probably be satisfied with the emissions inventory and the meteorology.

If the chemistry worked, you should get this result. I think we're pretty close to this.

WALKER: I have a couple of questions I want to direct to Dr. Whitten on a slightly different subject. I was pleased at your comment that the O_3-generation process appears to get more efficient as the reaction mixture dilutes. I've held this view for a long time.

I'd like to ask your thoughts on the hypothesis that really high levels of O_3 will not occur unless the mixture is diluted considerably.

Also, I'd like to ask, are there in these various mechanisms reactions that would lead to this performance, of changing the site reactions? Would you anticipate from the chemistry embodied in these models that you would get more efficient O_3 production as the mixture was diluted?

WHITTEN: One of the things that goes on in the efficiency effect is that radical-radical reactions go to the square of the concentration of radicals. As the radical concentration goes down, these reactions drop out because they're important to the square.

However, they don't seem to be important under a wide range. A few years ago they were felt to be much more important. Another example is the formation of nitrates. The OH-NO_x reaction, and reactions like it, slow down as the NO_x go down to lower and lower concentrations. This is a major sink in the chemistry of these.

Thus, you go to low NO_x concentrations, and the radicals don't disappear. The steady-state concentration of radicals can still remain very high, so you have a lot of radicals to work with in relationship to the amount of pollutants there are. The cycle rate around can still be very high, so you get very high efficiency.

One of the ways you can characterize how much O_3 you make is to keep this NO-to-NO_2 conversion going until you run out of NO_x. The speed at which the NO_x runs out is proportional to the amount of radicals that are around.

The mechanism then says how much O_3 you can make on this NO-to-NO_2 conversion rate before you run out of NO_x.

The current mechanism in the EKMA model has lots of rate constants that could be updated. The systems approach, if you want to use that word, could also be used to greatly improve the performance of EKMA by one little adjustment in the ratio of the HO_2-to-NO conversion to the OH + NO_2 reaction; in other words, this conversion rate to the loss. If you make that adjustment, it starts performing like a lot of other modern mechanisms.

Now, that's the only adjustment we needed to close the major gap in performance. We made it equal of the modern ratio without changing all those other rate constants.

If you change one rate constant indiscriminately and not the others, you upset the apple cart. You can change everything, or maybe just this one ratio.

JEFFRIES: But, Dr. Whitten, when you change that ratio, you increase the reactivity of the system. What you have to do is compensate for that increased reactivity by readjusting the propylene-butane split so that now those factors fit the smog chamber data it was used on before. I suspect in some of the studies you've done with the Carbon Bond mechanism, the numbers are like 10% and 90% instead of 25% and 75% once you change that rate constant.

WHITTEN: Either that or as Dr. Dodge has indicated in the original smog chamber modeling work of the Bureau of Mines, there were some assumptions as to pollutants coming off the walls, the chamber effects, and--

JEFFRIES: No, that's not significant compared to the O_3. You have to get the ppm of the material; for example, instead of making 0.3 ppm of O_3, make 0.5 ppm of O_3; that is what the Carbon Bond mechanism does. That's what Carbon Bond does with 25% and 75%. You make Carbon Bond 10% and 90%; it's much more. To match the Dodge mechanism as you change that--

WHITTEN: I was addressing a point made by Gerald Gipson that if there were a change in the mechanism so that it looked more like the Carbon Bond mechanism, it wouldn't fit the Bureau of Mines chamber anymore.

JEFFRIES: The 25%-75%, it might not.

WHITTEN: That's true.

KELLER: What was your answer to his question about absolute dilution? You actually make more O_3 by diluting the emissions; the efficiency goes up but the absolute amount of O_3 doesn't.

WHITTEN: Right. The answer to that is seen in the atmosphere. First of all, the Appendix J curve originally showed that quite clearly. If you take the most modern mechanisms now and look at the O_3 generated from HC along a potential maximum, it looks like the Appendix J curve.

What happens at the higher concentrations is that you have a lot of NO_x around and the radicals are held down. The efficiency of converting NO to NO_2 before you run out of NO_x goes down because there is so much NO_x present that the radicals in proportion are very low in concentration compared to the pollutants. So the cycle time is relatively slow compared to what it is at the lower concentrations.

KELLER: But the dilution shouldn't change. The HC:NO_x ratio is going to affect whether the radicals terminate, react with NO_2, propagate, or react with the HC. But dilution, just dilution, per se, shouldn't affect that composition.

WHITTEN: I guess what Harry Walker said was that possibly dilution was necessary to generate higher levels of O_3.

WALKER: That is a phenomenon everybody is aware of, that the highest levels of O_3 are always 15 to 20 mi out and not at the point where the most pollutants are.

I know this is part of the analysis phenomenon, but I wonder to what extent this dilution factor is involved in that.

WHITTEN: Well, the effect of dilution has been shown in smog chamber experiments, and also with the mechanisms and models, to be less than linear. Diluting a smog mixture by a factor of two doesn't cut down on the amount of O_3 by a factor of two. So, in a sense, dilution makes it more efficient, or in another sense, it helps.

Certainly, however, you can conduct a smog chamber experiment with a lot of undiluted materials and produce plenty of O_3. So, I don't think it is totally a necessary amount.

WALKER: Dr. Whitten, I have a second question that concerns the initiation process. The radical reactions you gave were dependent either on HONO, aldehydes, or O_3.

Now, if you don't have an aged air mass, you have a relatively one-pass air situation. In our analyses of Houston air, we certainly never found many aldehydes. I wouldn't think there'd be much HONO, to go along with it, as far as aged air. That's been much of the reason I think of background O_3 as being a factor of the initiation process.

WHITTEN: I didn't mention the O_3-olefin reaction which is possible.

WALKER: Yes. Well, it was mentioned in your list. But, the key point is the dramatic initiation of episodes we have, much more so in Houston than in Los Angeles, and what starts the process?

I realize higher concentrations can start the process, but is there anything in the chemistry that is built into these models that would make increased concentrations _per se_, that would become a source of radicals to begin the whole thing?

WHITTEN: There are inklings of something fishy going on in that area that we don't understand.

Harvey Jeffries has done some experiments where he spiked the mixture with O_3 or titrated the NO with O_3. He then compared the results with those obtained by simply putting NO and NO_2 in the smog chamber at the same ratio. There was a certain lack of reproducibility between those two things.

The chemistry, as we know it, is very simple and straightforward. It says there is really no effect between those two processes whether you have NO_2 naturally or whether the NO_2 comes from NO reacting with O_3. Dr. Jeffries is considering looking at this again.

If you took most of the mechanisms and models we currently have and spiked them with O_3, there is really nothing at the moment that says that it is going to suddenly take off, other than the effect of the NO_2 ratio. It is not written off but it's not obvious what it is.

JEFFRIES: I would like to return to the point that Dr. Dimitriades was making about the testing of the mechanisms in the atmosphere. What we are dealing with here, and what has become pretty clear procedure over the last couple of years, is in effect a hierarchy of tests. I think that if one were constructing a mechanism today, as opposed to 1976 or 1979, it would be like the lawyer with himself for a client if he didn't use the data available on chemical kinetics in constructing that mechanism to begin with.

There is no reason to believe that a mechanism that has known kinetic deficiencies is going to be reliable. Even if it does fit the smog chamber data, it is suspect from the very beginning. So, you begin by constructing a mechanism that's based on known information at the time.

Next you'd want to see whether or not that mechanism can reproduce the experiments in which only chemistry is the major driving factor. Often you separate out all the temperature and light effects and everything else by going through a chamber in which those things aren't changing. Once you can do that, you can start looking at behavior in systems where light, temperature, and humidity are changing and so forth.

Then you begin to find things wrong with the data and the model, and you fix them, and do the whole thing over again, which is why there is always a need for more smog chamber data.

In the end, you test the model in the ambient atmosphere, and it either works or it doesn't. If it doesn't work, you have lots of places to go to look for the answer. The answer may be that the chemistry in the smog chamber is not adequate for the kinds of conditions you're seeing in the ambient environment. If so, you go back to the smog chamber and run those experiments over again under conditions that are more appropriate for the behavior that you're looking at.

So, it's a clear hierarchy of applications, testing, recycling, etc., etc. There is no one suitable test I can give anyone to determine whether the model's mechanism's performance in one situation means it's okay. It is a complicated, long process that involves constant incorporation of new information.

I think for that reason a lot of people who aren't in the modeling community get really upset with modelers because they're constantly changing things. That's the problem with the regulation end of things. How does the regulator say this model is satisfactory and this model is not?

WHITTEN: I think everything you say is essentially true, but I still think that there can be some standard tests set up that say if you can't do this, then you can't play the game. You're going to find some people who say we can't do that but that's not a good test. That is an adequate response, too. If you have a good legitimate reason for saying this particular set of smog chamber data is really bad and you can prove it, because you've got this other set that's better, that's also still possible.

JEFFRIES: Fine, I agree with that.

CARTER: I'd like to add a third comment. I don't think it is a good idea for the government to specify the test we have to follow. There may be disagreement. The people who work on them are the best judges of what types of test should be used.

The mechanism I developed reflects the knowledge of the chemistry in 1979. I have also been doing calculations on models, essentially the model of Atkinson and Lloyd, which represents 1980 and 1981 chemistry. At least during that period, I found very little change essentially, 10% difference in the O_3. In that period there wasn't any great change. It looks like they're beginning to converge on the proper chemistry.

Finally, I think I remember your mentioning earlier that there is some evidence now that there is initial HONO emitted to some extent in the atmosphere, so there might be some initiation of HONO either being emitted or being formed by some unknown dark reaction. I don't think it's the only thing that starts it off, but I think it may possibly contribute.

WHITTEN: Yes. We've added HONO to our models. The airshed model has had it in it for several months, since we heard about it.

CARTER: Yes, you did.

WHITTEN: It makes some difference, especially on the first day of a 2-day simulation. But on the second day, you don't see much of an effect because the aldehydes tend to be higher on the second day; they build up.

The effect is in the first hour of the day when the sun comes up, but that carries over throughout the day.

KILLUS: I would have to say that I am extremely pessimistic about the notion of validating chemical mechanisms in the atmosphere.

If we take the various chemical mechanisms available right now and run them under similar conditions and compare the results, we get differences, 10% or 20%. In fact, a difference as large as 50% usually means that you've mispunched a card somewhere and might have put in the wrong rate constant.

If, on the other hand, you look at comparisons of models to the atmosphere and for that matter, if you look at just general variability in the atmosphere, what do you see? You see that your HC input data are unknown to factors of 2 or 3. You see that a shift in wind direction by 10 to 20% can give you orders-of-magnitude difference in your O_3 concentration. You see differences in mixing depths that cannot be estimated from currently known meteorology or methodology. Those areas are much more uncertain than the present chemistry, and are far in excess of the present chemistry.

I quite agree with Dr. Jeffries that there may very well be differences in smog chamber phenomena and differences in the chemistry in the atmosphere.

There are certainly differences in the kind of background phenomena that you see. But, those effects are still extremely small compared to the enormous meteorological uncertainty, the enormous uncertainty in emissions inventories and speciation in general, i.e., carryover phenomenon.

I can't imagine anyone comparing two mechanisms and saying, because this mechanism seemed to work better in St. Louis or Denver or Sacramento or Houston or Los Angeles, this mechanism is better and is giving more realistic chemistry than the other mechanism. It's almost certainly going to be some other variable in the computation.

9. EFFECTS OF CHEMISTRY AND METEOROLOGY ON OZONE-CONTROL CALCULATIONS USING SIMPLE TRAJECTORY MODELS AND THE EMPIRICAL KINETIC MODELING APPROACH PROCEDURE

H.E. Jeffries
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[Editor's Note: The text of this presentation has been published previously and is available as an U.S. Environmental Protection Agency report:

> Jeffries, H.E., K.J. Sexton, and C.N. Salmi. 1981. Effects of Chemistry and Meteorology on Ozone-Control Calculations Using Simple Trajectory Models and the EKMA procedure. EPA-450/4-81-034, U.S. Environmental Protection Agency, Research Triangle Park, NC (November).]

WORKSHOP COMMENTARY

ESCHENROEDER: I have a couple of comments, Dr. Jeffries, and then a question. First of all, I question why you insist on exact prediction and how this affects the percent reduction. It's my understanding that the precursor concentrations are only used to get the ratio line, not a starting point, on the EKMA diagram.

It seems to me there is only one way to use it--lay the ratio line through an observed O_3 level and proceed from there, accepting that the air mass that was at this point as a precursor measurement doesn't exactly represent the air mass in which that O_3 level was observed.

I'm not really concerned with that. In fact, I might average precursor concentrations over several days to get the slope. So I really question whether that is a concern about EKMA.

Secondly, I think your stress on changes in O_3 to relative changes in precursors is one of the most important messages of your work, rather than absolute O_3 predictions from a model. Someone said this morning that all the models are within 20% of predicting O_3. I felt like saying, well, I guess all the chemists should go on a vacation for a couple of years. However, when you cast it in the light of Delta O_3 per Delta precursor, the situation isn't nearly so rosy.

I would like to preface my last question with the statement that when I read your paper on the way here, I almost wished I hadn't come because it looked like such an insuperable problem.

In view of what you know, how would you advise a control agency with limited data to proceed? You have, very correctly, taken scenarios available from the literature, any of which could conceivably be legitimately used by control agencies in justifying a stiff decision. How should we proceed?

JEFFRIES: The emphasis in Level II is on absolute prediction. That was the fundamental basis for the funding of our work, the issue of absolute prediction.

The idea at Level II is to achieve an absolute prediction. That is one of the primary differences between an isopleth diagram generated at Level III and an isopleth diagram generated at Level II. In Level II you should be putting in the best description you have of the chemistry, the best description you have of the meteorology, the best description you have of the trajectory, and all of these other factors.

ESCHENROEDER: So you tell the agency to strive for Level II.

JEFFRIES: No. The Agency decided in 1979 that there were four levels and the second level was the one we were testing. That was a probable recommendation to the states for calculating SIP's. That level is an absolute prediction level.

So part of this was to see whether if you go to Level II the method will give you good answers. Are the answers dependent upon the chemistry and the meteorology? My answer to these questions is, absolutely.

If you fall back on Level III, that is, if you use the method in a relative sense, you fall into the trap of the correlation between the isopleth's facing and the actual HC number obtained where the HC:NO_x ratio line intercepts the O_3. The further out that is, the lower the control requirement. The closer to the origin it is, the higher the control requirement.

ESCHENROEDER: I see what you mean.

JEFFRIES: Thus, one has difficulty using it in an absolute sense because you've got to specify the meteorology in the physical modeling conditions better, and one has difficulty using it in the relative sense because the degree of control is proportional to absolute prediction.

The better you predict, the closer the control. Still, however, different mechanisms when predicting correctly give different absolute HC, Delta O_3, and Delta HC values.

If you abandon EKMA as a correction method when your model doesn't give you the right answer and go to absolute models with absolute predictions, you are still stuck with the same problem. How does the model say Delta O_3 per Delta HC goes?

Also, different models give you different Delta O_3 per Delta HC. Furthermore, O_3 aloft is a dominant factor. It is the fifth highest day of the year that is the real day for control in St. Louis, not the highest day. That means the control on that day is the function of how the mechanism treats that entrained O_3. The mechanisms weren't developed to deal with entrained O_3.

We observed that the answer lies somewhere in between 1:1 and 2:1, if you believe the chemistry. So one of the things to do is to take your control diagram and draw a line that's 1:1, and use that as one bound, and draw another line on there that says the O_3 changes twice as fast as the HC and use that as the other bound. Then you can run a lot of models and see where they cluster, and then make your choices from that range of answers.

There is a fair amount of uncertainty in where we're going.

ESCHENROEDER: It sounds like you're saying we don't need more research, we already have almost too much research, because there are so many different--

JEFFRIES: No. We clearly need models that can model more accurately, that have data bases to test the models on all the factors that are important in the atmosphere, and that haven't been used in the smog chamber.

It is possible to put a model together in a smog chamber that can't model the atmosphere at all, because the factors that control O_3 in the smog chamber on that side of the surface aren't the factors that control O_3 in the ambient environment.

Dilution and emissions are the dominant factors in the ambient environment. When the lights are turned off, dilution is also the dominant factor in the smog chamber. Thus, radical sources in the smog chamber that can change the speed of the radical initiation process, are going to control the smog chamber.

We haven't had the data bases to test the models. The models may be okay. We don't know. What we do know is that the models are different.

ESCHENROEDER: That is what disturbs me. You have no data base now, you are saying, on which to choose one or the other model.

JEFFRIES: No, what we have to do is go back to what I said before. You start out by going through the model and validating all the gas-phase fundamental kinetics we know.

This is Dr. Carter's point. You go back to the beginning, and you realize that all the numbers used in the model when it was first put together aren't the right numbers here. So you have to reconstruct those numbers. Then you model certain sets of data that you can say, yes, for these conditions, it works. Then you continue to build that up. What we don't have are those kinds of conditions to exercise the models against.

Now, even when you get through doing all of that, there may be another problem. Radical sources in the atmosphere may be totally different from radical sources in the smog chamber. That's the whole question of the HONO measurements.

If the model can characterize a smog chamber well under dynamic conditions of dilution, injection, O_3 aloft, and so forth, and you apply that model to the atmosphere with the best meteorology data you have, and it still doesn't work, there is something else going on in the atmosphere that you don't have going on in the smog chamber.

LLOYD: Dr. Jeffries, do you see anything inherent in the chemical mechanisms which would lead you to believe that when you inject O_3, you entrain O_3 aloft?

JEFFRIES: What happened here was simply that the mechanisms had different representations. Some included processes, some didn't. There were different deletions, different distortions, and different generalizations used to construct the mechanisms.

If all the mechanisms had been the same, they may have all treated it the same. No, I don't think there is anything funny about what's going on. I think we haven't had to deal with that.

LLOYD: What do you mean by treating it differently? We've got O_3 reacting with olefins, O_3 reacting with NO. How--

JEFFRIES: Some researchers photolyze the O_3, some researchers don't. Some have it reacting with a lot of things, and some don't.

LLOYD: What do you mean, a lot of things, besides the NO and the O_3?

JEFFRIES: The answer to that is get out the mechanisms and look at all the O_3 reactions that are in them. All the loss mechanisms for O_3, the loss processes for O_3, are not the same in four different mechanisms that we looked at. That's the issue.

For example, for the question of deposition, all those things are not there. Whether a model includes or doesn't include deposition will influence how much of this entrained O_3 gets reactive in different places.

It is just a matter of different people making different choices in these three areas when they put their models together. You can't point to one and say, that's wrong. It may have been that for the conditions they tested, the model for what they had was quite adequate. But, that is not the case here. The smog chamber they tested it on didn't have O_3 injected in in throughout the whole day.

It might turn out that if you had a data base for a smog chamber in which we injected O_3 all day, and you ran a model against it, it might work. Some mechanisms didn't include processes to account for all of the possible O_3 behavior when O_3 was going to be entrained into the parcel; others put different things in that did cause differences.

What I can say is when we ran the models for the same conditions, they gave different answers. That is because different choices were made in constructing the model. I'm not saying one of those choices was good or bad. Different choices were made by different reasonable people.

McRAE: I have two quick questions. Would you care to put your last slide back on and take a crack at what you think might be the criterion?

One of the things we've found in our work is that simply comparing the absolute predictions at any given time leads to false interpretations. For example, if you have a 1-h peak shift, for an extraordinarily well-defined peak, just that 1-h shift can give you rapid changes in scatter plots that can give you very meaningless answers.

JEFFRIES: That's why I got away from the scatter plots as fast as I could, and why the report is full of actual plots of data versus data. The problem is you get a very voluminous quantity and people like Ned look at it and say, what does all this mean? Scatter plots are one way to do it, but they have to have all sorts of hooks attached to them that say, read these and caution.

Many people got upset over the scatter plots for the Bureau of Mines, and we received a lot of comments on that. As a consequence, I revised a lot of the text. I'm still not happy with it. But, I agree with you. One of the reasons a lot of this didn't come out before was that the kinds of data plots we were doing hadn't been done in some of the previous studies where all they did was look at the peak O_3. It looks pretty good on the basis of peak O_3.

When you actually look at the degree of predictions and look at the precursor predictions, and so forth, they don't look very good. So, I agree with you.

McRAE: My second question is, have you tried any multiday runs to help characterize the O_3? One of the major conclusions you made was that the control requirements are critically dependent upon the level of entrained O_3. That is a pretty difficult parameter to specify for the agencies because they don't have access to that kind of information.

What happens if you do the multiday runs on some of these trajectory models? Have you looked at the amount of O_3 that's left aloft at the end of those days?

JEFFRIES: No, the model doesn't have the structure to do that. It really doesn't. The mixing height is always rising and that's it. It may stop and not go up, but nothing ever happens after that. So they don't even have the ability to handle the collapsing and mixing height of the entrainment. It's a respecification problem.

So, if you ask where the 0.12 ppm O_3 came from that we entrained on Day 159, well, if you believe all of the other data from St. Louis, it came from 250 mi upwind.

WHITTEN: The OZIPP model has the ability to come back in.

JEFFRIES: No, we weren't using OZIPP. We didn't look at 2-day O_3, is a short answer to your question.

DERWENT: Can you put that slide back up. I am interested that you might have a criterion which tells you whether the model representation of Delta O_3 over Delta HC is, in fact, what happens in the atmosphere.

Could you answer a question? Do you think if the models were made more complex or more complicated, it would be easier to find a criterion which would tell you whether that answer was more or less realistic?

Because the models are simplified, does that mean it's more difficult to find a criterion? If the models were better representations of atmospheric processes, would that criterion be easier to find?

JEFFRIES: I think the models are going to become more complicated, though one or two are not. I also think what we'll end up doing is having a range of complicated models that will allow us to capture the process. Then we're going to model the model, that is, get a simple model to feed back into the very complex airshed models.

My intuition tells me that the models are going to get more complicated, more complicated in the sense that they have a better chance of representing various pieces and are likely to do a better job. Again, the thing a model must be able to do is describe reality in some sense, and what we're missing is, what's reality. We don't know what the O_3 is as a function of aromatic changes from 25% to 45%, da da ta da.

I suspect that to do all these things the models are going to become complicated. Because, we're going to stick all these things into the model to generate the behaviors we want to observe.

Look at O_3 aloft. Most people could leave out some of the O_3 chemistry that is included in many models because in an urban-type smog chamber simulation, that is not important. But, for entrainment aloft and low concentrations in the ambient air, it is important. So, people take it out because it's not important in that condition. Then they go and apply the model some place where it is important. It's one of those things where, as Dr. Whitten said before, you go through and trim. You write all this out and you run it against your data base, and you say, well, that doesn't make any difference, I'll take it out. You keep doing this. But, when you apply it some place where one of those things may make a difference, you have to be very careful. So, yes, the models are going to get more complicated.

MEYER: I would like to comment a little on that last point. One of the things we have been doing is attempting to compare the control predictions one gets with the simple models versus those one gets with the urban airshed model, using the Carbon Bond II mechanism, and so on.

We've looked at several days, and, generally speaking, the ranges one gets, the discrepancies one gets between the simple models and the air shed control predictions, are nowhere near as large as the ranges which Dr. Jeffries was talking about in some of these calculations. Thus, there may be, indeed, some promise in doing a number of simulations with the complex models and perhaps using those as a criterion for how well the simple models perform.

The one major fallacy with that is, you're not entirely sure that the complex models are predicting what's going to happen with the strategies correctly, either.

ESCHENROEDER: Also, those comparisons contain implicitly the same sets of assumptions about mechanism mixing height and all that and they agree very well, as Dr. Whitten showed yesterday. When you start going to other more reasonable sets of assumptions, you get much larger disparities than those comparisons indicate. Because that is a model versus model comparison, and they come from the same data base.

10. EFFECT OF RADICAL INITIATORS ON EMPIRICAL KINETIC MODELING APPROACH PREDICTIONS AND VALIDATION

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ABSTRACT

This paper discusses the impact of uncertainties concerning radical initiators in smog chambers and urban atmospheres on Empirical Kinetic Modeling Approach (EKMA) predictions. It presents evidence that both initial nitrous acid and continuous nitrogen dioxide-dependent radical sources are important in smog chambers, and must be taken into account when validating kinetic mechanisms for use in EKMA calculations. Presently, the extent to which the nitrogen dioxide-dependent chamber radical source operates in the open atmosphere is unknown. The paper examines the effect of this uncertainty on calculated ozone isopleths and predicted EKMA control strategies. Since ambient nitrous acid recently has been observed in the early morning at sites in Los Angeles, the paper also examines the effect of varying initial nitrous acid concentrations on EKMA simulations. In general, increasing radical initiation results in higher predicted ozone yields at high oxides of nitrogen:hydrocarbon ratios, while not significantly affecting the predicted ozone when the oxides of nitrogen:hydrocarbon ratio is low. This increases the degree of hydrocarbon control predicted in EKMA analyses to be required to achieve specified ozone reductions.

INTRODUCTION

The Empirical Kinetic Modeling Approach (EKMA) can be a useful technique for obtaining quantitative ozone (O_3)-precursor relationships, provided that its inherent limitations and the ranges of uncertainty in its predictions are adequately understood. Many of the uncertainties and limitations of this technique have been discussed in detail elsewhere (EPA, 1977; Dimitriades, 1977; Dodge, 1977; Bilger, 1978; Carter et al., 1982; Hov and Derwent, In press; Whitten, In press; Jeffries, 1981); in this paper we restrict discussion to uncertainties concerning radical initiators and the effect of these uncertainties on EKMA predictions. Recent sensitivity calculations (Carter et al., 1981; Hov and Derwent, In press; Jeffries, 1981) show that the results of EKMA calculations differ significantly when one uses different kinetic mechanisms or different representations of the composition of the reactive organics, even if one uses the "relative" isopleth analysis technique (EPA, 1977; Dimitriades, 1977). However, most of these calculations compare predictions of entirely different kinetic mechanisms or representations of reactive organics. Thus, the effects of uncertainties in specific mechanistic features or specific reactivity characteristics of the initial or emitted species, such as those related to radical initiation, could not be determined.

The major areas of uncertainty related to radical initiation that this paper discusses concern the "chamber" radical source (Carter et al., 1979; Carter et al., 1981; Carter et al., In press) and the effects of a known photoinitiator, nitrous acid (HONO), on EKMA predictions. Many investigators have long realized that model calculations significantly underpredict rates of oxides of nitrogen (NO_x) oxidation and hydrocarbon (HC) consumption in smog chamber experiments if the model does not provide for radical sources beyond those provided for by the known homogeneous reactions of measured (or upper-limit) levels of known photoinitiators (Carter et al., 1979; Hendry et al., 1978; Falls and Seinfeld, 1978; Whitten et al., 1979; Whitten et al., 1980). Modelers disagree about how to account for this discrepancy. Some assume that the discrepancy results from the presence of initial HONO (formed heterogeneously when NO_x are injected) (Falls and Seinfeld, 1978; Whitten et al., 1979; Whitten et al., 1980); some assume it results from continuous input of hydroxyl (OH) (Carter et al., 1979) or hydroperoxyl (HO_2) radicals (Hendry et al., 1978); and some assume a combination of both (Hendry et al., 1978). These approaches differ significantly. The use of initial HONO alone leads to a rapidly decreasing radical flux over the time scale of 30 min to 60 min, whereas a continuous radical source results in a considerably greater total radical input during a typical 6-h to 10-h smog chamber irradiation. Since the kinetic mechanisms used in EKMA models are generally validated against smog chamber data, this discrepancy represents an important uncertainty in EKMA predictions, particularly since aspects of the mechanism related to radical initiation and termination can not be tested unambiguously.

In addition to the uncertainties in model validation caused by poorly characterized chamber radical sources, no one has adequately considered the possibility that some of the factors causing these sources may operate in the open atmosphere. Indeed, Harris et al. (In press) have observed up to 8 ppb

HONO in a Los Angeles source area, indicating that initial HONO is a factor in the ambient air as it is in smog chamber simulations. In addition, recent data discussed in this paper suggest that at least some of the factors causing the continuous nitrogen dioxide (NO_2)-dependent radical source observed in smog chambers may also be important in the open atmosphere. This paper discusses the evidence for the existence of the chamber-dependent radical source, and the possibility that there are also unknown atmospheric radical sources. It also examines the effect of initial HONO and of an unspecified NO_2-dependent radical source on EKMA predictions. The results help to characterize the sensitivity of EKMA predictions to uncertainties concerning radical sources.

EXPERIMENTAL STUDIES OF RADICAL SOURCES IN ENVIRONMENTAL CHAMBERS

Four different environmental chambers were employed in our studies of radical sources. The majority of irradiations were carried out in the SAPRC 5800-liter evacuable, thermostatted, Teflon-coated environmental chamber equipped with a 25-kW solar simulator (Winer et al., 1980). Experiments in this chamber were performed at a variety of temperatures (282°K to 325°K), humidities (dry to ~100% RH), total pressures (~350 torr to atmospheric), and light intensities (k_1, the NO_2 photodecomposition rate, = 0.25 to 0.5 min^{-1}). A more limited set of irradiations were carried out in the SAPRC ~6400-liter indoor all-Teflon chamber, with irradiation provided by two diametrically opposed banks of 40 Sylvania 40-W BL lamps, backed by arrays of Alzak-coated reflectors. All runs in this chamber were performed at ~300°K, but the humidity was varied from < 10% RH to ~50% RH, and the light intensity was varied from $k_1 \cong 0.1$ min^{-1} to $\cong 0.45$ min^{-1}. A number of irradiations were also carried out in ~40,000-liter outdoor Teflon-bag chambers with natural sunlight irradiation (Carter et al., 1981). In these experiments, the temperature varied from ~320°K to ~340°K, humidity from < 10% RH to ~50% RH, and light intensity from $K_1 \cong 0.25$ min^{-1} to $\cong 0.4$ min^{-1}. Irradiations were performed in new, newly conditioned, and extensively used bags. Finally, a few irradiations were carried out using ~100-liter Teflon bags irradiated with an array of fluorescent lamps yielding an NO_2 photolysis rate, k_1, of 0.27 min^{-1}. In this system, the temperature was held at ~300°K, and ultra-high-purity dry air was used. It should be noted that the ~100-liter, ~6400-liter, and the ~40,000-liter Teflon chambers employed in this program were all constructed from the same roll of 2-mil thick, FEP Teflon film. The characteristics of these chambers and the associated experimental operating procedures are described in detail elsewhere (Carter et al., In press; Winer et al., 1980; Carter et al., 1981; Pitts et al., 1979), and thus are not discussed further here.

The experiments performed consisted of monitoring radical levels in NO_x-air irradiations in which the levels of organics were kept sufficiently low that their effects on the NO_x-air reactions would be minor. In such a system, the major gas-phase reactions (Carter et al., 1979; Hampson and Garvin, 1978; Baulch et al., 1980; Atkinson and Lloyd, 1980) are as follows:

$NO_2 + h\nu\ (\lambda \geq 295\ nm) \rightarrow NO + O(^3P)$ (Reaction 1)

$O(^3P) + O_2 + M \rightarrow O_3 + M$ (Reaction 2)

$NO + O_3 \rightarrow NO_2 + O_2$ (Reaction 3)

$O(^3P) + NO_2 \rightarrow NO + O_2$ (Reaction 4)

$O(^3P) + NO_2 \overset{M}{\rightarrow} NO_3$ (Reaction 5)

$NO + NO + O_2 \rightarrow 2\ NO_2$ (Reaction 6)

$NO_2 + O_3 \rightarrow NO_3 + O_2$ (Reaction 7)

$NO_3 + NO \rightarrow 2\ NO_2$ (Reaction 8)

$NO_3 + NO_2 \rightarrow NO + NO_2 + O_2$ (Reaction 9)

$NO_3 + NO_2 \overset{M}{\rightarrow} N_2O_5$ (Reaction 10)

$N_2O_5 \overset{M}{\rightarrow} NO_2 + NO_3$ (Reaction 11)

$NO_3 + h\nu \rightarrow NO + O_2$ (Reaction 12)

$NO_3 + h\nu \rightarrow NO_2 + O(^3P)$ (Reaction 13)

$O_3 + h\nu \rightarrow O_2 + O(^3P)$ (Reaction 14)

$O_3 + h\nu\ (\lambda \leq 310\ nm) \rightarrow O_2(^1\Delta g) + O(^1D)$ (Reaction 15)

$O(^1D) + M \rightarrow O(^3P) + M$ (Reaction 16)

$O(^1D) + H_2O \rightarrow 2\ OH$ (Reaction 17)

$OH + NO \overset{M}{\rightarrow} HONO$ (Reaction 18)

$HONO + h\nu \rightarrow OH + NO$ (Reaction 19)

$OH + NO_2 \overset{M}{\rightarrow} HNO_3$ (Reaction 20)

In these experiments, nitric oxide (NO) levels were kept sufficiently high so that significant O_3 formation could not occur, and thus reactions 7 through 17 were of minor importance. In particular, the OH radical input rate calculated from the above mechanism is ~4 x 10^{-6} ppm min^{-1} for conditions of a 50% RH evacuable chamber run where [NO] = [NO_2]. This gives rise to predicted OH radical levels one to two orders of magnitude lower than those observed (see below).

We also included in the reaction mixture added traces ~< 10 ppb) of propene and propane (or propene and n-butane) in order to monitor OH radicals from their relative rates of decay. The use of two tracers instead of one has the advantage that OH radical levels can be related only to changes in their concentration ratios (see below), which can be experimentally measured with more precision than changes in absolute concentrations. Under the conditions employed in these runs, reaction with OH radicals is the only significant mode of consumption of n-butane, and it is the major reaction consuming propene. However, under some conditions, consumption of propene by reaction with O_3 and $O(^3P)$ is non-negligible, and a correction must be made. When [NO] >> [O_3], as is the case for all of the experiments discussed here, OH levels can be derived using Equation 10-1:

$$[OH] = (k_a - k_b)^{-1} \quad \frac{d \ln \frac{[propane]}{[propene]}}{dt} - \frac{k_1 k_c \, [NO_2]}{k_3 \, [NO]} - \frac{k_1 k_d \, [NO_2]}{k_2 \, [O_2] \, [M]} , \qquad \text{(Eq. 10-1)}$$

where k_a and k_b are, respectively, the rate constants for the reaction of OH with propene and propane, k_c and k_d are rate constants for the reactions of propene with O_3 and $O(^3P)$, and k_1 through k_3 are the rate constants for reactions 1 and 3. The second and third terms in the above equation are the corrections for the consumption of propene by reaction with O_3 and $O(^3P)$ and are derived (Carter et al., In press) by assuming that $O(^3P)$ and O_3 are in a photostationary state. This correction is < 10% when $[NO_2] \sim< 0.3$ ppm and $[NO]/[NO_2] > 1$, which is the case for most of our experiments.

The presence of the propene or propane tracers at the < 10-ppb level in these NO_x-air irradiations has a negligible effect on the NO_x chemistry and radical levels, except that they cause a slight increase in the conversion of NO to NO_2 (Carter et al., 1979; Carter et al., In press; Atkinson and Lloyd, 1980). (At the reactant levels employed in these runs, the rate of this conversion is minor, being generally less than the conversion caused by the reaction of OH with the carbon monoxide (CO) impurity (0.5 to 4 ppm) that passes through our air-purification system.) In particular, although the reaction of propene with O_3 and $O(^3P)$ and the photolysis of the oxygenated products formed from the reactions of the tracers can lead to radical production, these radical sources are minor at the reactant levels employed in these runs (Carter et al., 1979; Atkinson and Lloyd, 1980).

For this tracer technique to be valid, the observed changes in the propane:propene ratio must be shown to actually reflect the presence of radicals, and to not be caused by heterogeneous or other unknown loss processes for propene in these chambers. (The loss of propane was relatively slow in these irradiations, and primarily reflects dilution.) Repetitive pre-irradiation sampling has shown that no significant dark decay of propene (or of other simple HC's) occurred in our smog chambers, but this result does not rule out the possibility of light-induced heterogeneous decay. However, no evidence exists that light-induced heterogeneous decay of propene or other simple HC's is important in chamber systems, and there are a number of reasons to believe it is not. In the first place, a large number of OH rate constant ratios for organics, derived from their rate of decay in smog chamber irradiations, agree to within experimental uncertainty with values derived using entirely different, absolute techniques (Atkinson et al., 1979). This agreement could not be possible if a light-induced heterogeneous loss process were occurring in chamber systems at sufficiently high rates to account for the results of our tracer-NO_x-air irradiations. In addition, the rates of decay of the small n-butane impurity observed (in sub-ppb levels) in most of our irradiations were consistent with radical levels derived from the propane:propene ratio. Finally, note that if light-induced heterogeneous decay of propene were important, then all current propene-NO_x-air models (Carter et al., 1979; Hendry et al., 1978; Falls and Seinfeld, 1978; Whitten et al., 1979; Whitten et al., 1980) would be incorrect, since none have taken such a process into account.

Several control experiments were performed to further test the validity of the organic-tracer technique. One such experiment was based on a suggestion by Killus and Whitten (1981) and consisted of a NO_x-air irradiation in the evacuable chamber (< 10% RH, 0.4 ppm NO, 0.1 ppm NO_2) in which the propene/propane tracers were replaced by 50 ppm CO. The addition of CO causes the following reactions to become important:

$$OH + CO \xrightarrow{O_2} HO_2 + CO_2 \qquad \text{(Reaction 21)}$$

$$HO_2 + NO \rightarrow NO_2 + OH \qquad \text{(Reaction 22)}$$

These reactions result in no net change in radical levels, but they cause NO to be converted to NO_2 at a rate approximately equal to the rate of reaction (Atkinson et al., 1979). Thus [OH] can be derived from the following,

$$-\frac{d[NO]}{dt} \cong R_{23} = k_{23}\ [OH]\ [CO] \qquad \text{(Eq. 10-2)}$$

entirely independent of HC-decay rates. The NO-decay rate observed in this $CO\text{-}NO_x$-air irradiation was ~0.74 ppb min^{-1}, from which $[OH] \cong 0.9 \times 10^6$ molecule cm^{-3} (Eq. 10-2) can be derived. This is very similar to the average OH radical levels of $1.1 \times 10^6\ cm^{-3}$ derived from a 2-h NO_x-air irradiation carried out under the same conditions but with the organic tracers and no added CO. Thus the two techniques for measuring [OH] give consistent results.

An additional test to confirm that rates of change of the HC tracer ratio reflect radical levels was performed by determining if addition of known radical inhibitors would suppress these rates. Benzaldehyde was employed as the radical inhibitor, since it is known to inhibit O_3 formation in chamber irradiations (Gitchell et al., 1974; Atkinson et al., 1980), and the current mechanism for its NO_x-air photooxidation predicts that radicals are not regenerated following its reaction with OH (Atkinson et al., 1980). Thus a tracer-NO_x-air irradiation was performed in the evacuable chamber (< 10% RH, T = 303°K, NO = 0.4 ppm, NO_2 = 0.1 ppm). Approximately 1 ppm benzaldehyde was added to the mixture after a 2-h irradiation. The addition of 1 ppm benzaldehyde suppressed the rate of change of the propane:n-butane ratio by a factor of ~7 (Figure 10-1). The amount of suppression observed in this and other experiments using benzaldehyde agrees reasonably well with the amount of suppression calculated based on the known OH + benzaldehyde (Niki et al., 1978; Kerr and Shepard, 1981) and OH + NO_2 (Baulch et al., 1980; Atkinson and Lloyd, 1980) rate constants and assumed 100%-efficient inhibition by benzaldehyde. Thus, these control experiments, as well as others that will be described in a subsequent publication (Harris et al., In preparation), validate the tracer technique for monitoring radical levels.

The OH radical levels observed in all of the runs carried out were significantly higher than expected from the heterogeneous gas-phase reactions listed previously. These higher values can be seen in Figures 10-2 and 10-3, which show OH radical concentration-time profiles derived from the propene and propane decay rates observed in a representative standard evacuable chamber run (Figure 10-2) and from a representative high initial NO_2 concentration run (Figure 10-3) (Carter et al., 1982). These concentration-time profiles are compared with results of model calculations (curve A) using only the known gas-phase chemistry (where the largest single radical source

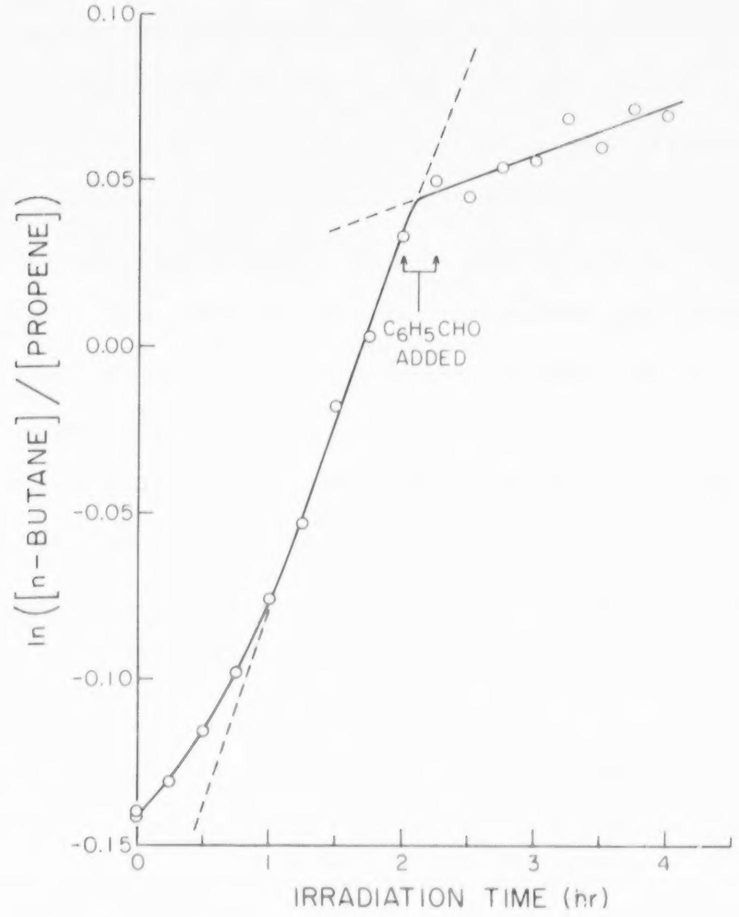

Figure 10-1. Plots of ln([n-butane]/[propene]) against time for the evacuable chamber run EC-623 in which benzaldehyde was injected during the run.

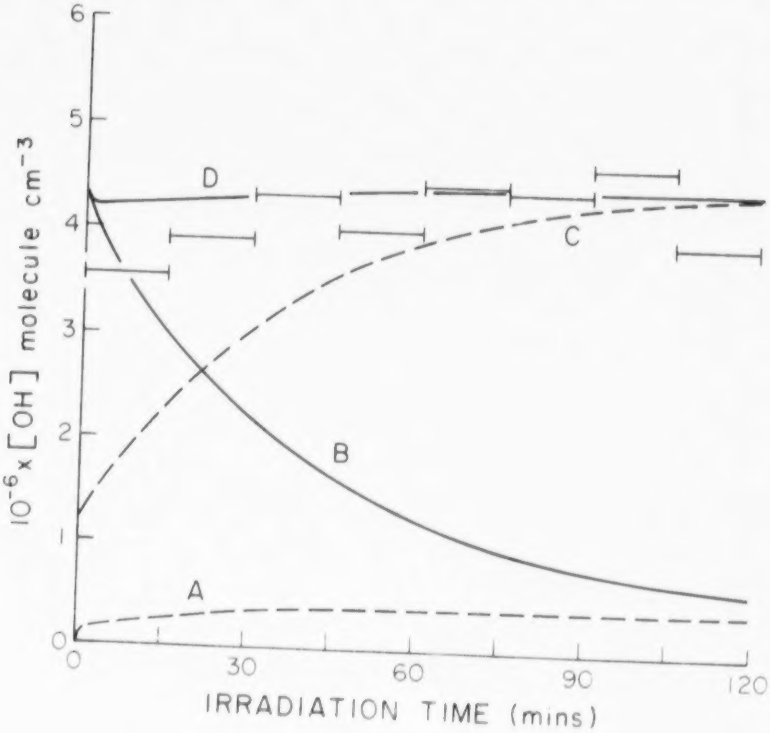

Figure 10-2. OH radical concentrations as a function of irradiation time. ---- represents experimental data for EC-457 (not corrected for the consumption of propene by reaction with O_3 or $O(^3P)$, which was minor); $[NO]_{initial}$ = 0.499 ppm, $[NO_2]_{initial}$ = 0.115 ppm; $[propane]_{initial}$ = 0.013 ppm, $[propene]_{initial}$ = 0.010 ppm; $[HCHO]_{initial}$ ≈ 0.020 ppm, T = 303°K, RH = 50%, NO_2 photolysis rate constant $K_1 = 0.49\ min^{-1}$; A - model calculations with the homogeneous gas-phase chemistry; B - model calculations with $[HONO]_{initial}$ = 0.010 ppm; C - model calculations with a constant OH radical flux of 0.245 ppb min^{-1}; D - model calculations with $[HONO]_{initial}$ = 0.010 ppm and a constant OH radical flux of 0.245 ppb min^{-1}.

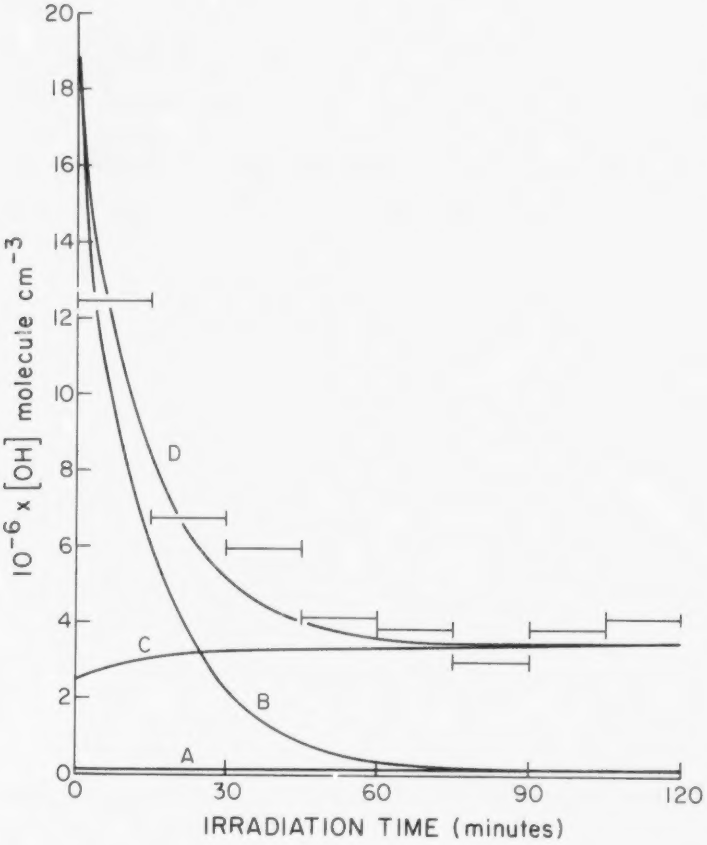

Figure 10-3. OH radical concentrations as a function of irradiation time. ---- represents experimental data for EC-442 (not corrected for the consumption of propene by reaction with O_3 or $O(^3P)$, which was minor); A - model calculations with the homogeneous gas-phase chemistry; B - model calculations with $[HONO]_{initial}$ = 0.050 ppm; C - model calculations with a constant OH radical flux of 0.61 ppb min^{-1}; D - model calculations with $[HONO]_{initial}$ = 0.050 ppm and a constant OH radical flux of 0.61 ppb min^{-1}.

was formaldehyde photolysis based on the observed initial formaldehyde levels of 20 ppb and 6 ppb, respectively), and assuming (1) only initially present HONO at levels adjusted to fit the initial OH radical concentrations (curve B), (2) a constant radical flux at rates adjusted to fit the final OH radical levels (curve C), and (3) a combination of both (curve D).

The known radical sources are clearly at least an order of magnitude too low to account for the observed radical levels in these runs, and assuming only initial HONO greatly underpredicts radical levels after the first ~15 min of the run, with initial HONO being, at best, only a minor contributor to the observed radical source after the first ~30 min of irradiation. On the other hand, using only a constant radical flux in the calculation results in an underprediction of the initial OH radical levels, especially in the high $[NO_2]/[NO]$ runs. The best fits to the data are obtained if some contribution from initial HONO is assumed. However, in terms of the overall input of radicals during a chamber irradiation (typically ≥ 6 h for smog-simulation runs), the continuous radical flux is by far the more important factor.

The radical flux required to fit the data for a given run can be estimated, without carrying out detailed model calculations, from the fact that radical-initiation and radical-termination processes must balance. Since the only significant radical-termination processes in this system are the reactions of OH radicals with NO and NO_2 (reactions 18 and 20), and since the only major known radical initiation process is HONO photolysis (reaction 19), then:

$$R_u + k_{19}\,[HONO] = k_{18}\,[OH]\,[NO] + k_{20}\,[OH]\,[NO_2], \qquad \text{(Eq. 10-3)}$$

where R_u is the radical-initiation rate from all sources other than HONO photolysis. Since known radical sources (other than HONO photolysis) are minor in these irradiations (see above), R_u is thus identified with the rate of radical input from unknown sources. Reactions 18 and 19 are the major reactions affecting HONO levels, so Eq. 10-3 can be rearranged to yield

$$R_u = \frac{d\,[HONO]}{dt} + k_{20}[OH]\,[NO_2]\ . \qquad \text{(Eq. 10-4)}$$

Furthermore, since the photolytic half-life of HONO in these experiments is $\leq$ 15 min (Atkinson et al., 1979), HONO can reasonably be assumed to be in photostationary state after the first hour. Therefore, the radical-initiation rates for $t > 60$ min in these photolyses can be estimated from the equation:

$$R_u(t > 60\ \text{min}) \cong k_{20}\,[OH]_{avg}[NO_2]_{avg}\ , \qquad \text{(Eq. 10-5)}$$

where k_{20} is accurately known (Whitten et al., 1980; Atkinson and Lloyd, 1980) and $[OH]_{avg}$ and $[NO_2]_{avg}$ (the average OH radical and NO_2 concentrations for $t > 60$ min) are experimentally determined. Note that, in general, the OH radical levels were approximately constant after the first hour of irradiation.

The radical-initiation rates derived using Eq. 10-5 were found to be dependent on the chamber employed and, to some extent, on the chamber history, and were proportional to light intensity, increasing significantly with temperature, humidity, and NO_2 concentrations. On the other hand, these rates were totally independent of the total pressure and NO levels (Carter et al., In press). The dependence of this radical flux on $[NO_2]$ and humidity (at $T \cong 303°K$ in the evacuable chamber) is shown in Figure 10-4. A monatonic increase in the radical source with increasing $[NO_2]$ can be observed, with the rate of increase depending on humidity. However, the data are such that whether the dependence is linear (as indicated by the least-squares regression lines), or whether, as some of the data points suggest, there is significant curvature at both high and low $[NO_2]$ levels is unclear.

The radical flux depended somewhat on chamber conditioning. For the ~40,000-liter outdoor Teflon chambers, NO_x-air irradiations were performed when the chamber was newly constructed, after it was "conditioned" by irradiation of ~0.5 ppm each of propene and NO_x, and after it was extensively used in a series of NO_x-air irradiations of ~25 ppmC aircraft or motor-vehicle fuels (Carter et al., 1981). The radical flux was found to be non-negligible even in new chambers, and did not increase measurably after propene-NO_x conditioning, but it did tend to increase (by factors of ~1.5 to ~3.5) following extensive conditioning by fuel-NO_x runs. On the other hand, for the evacuable chamber, when a NO_x-air irradiation was performed immediately after the chamber was "cleaned" by an overnight evacuated bakeout at ~360°K, the radical input rates were higher than those following other NO_x-air or

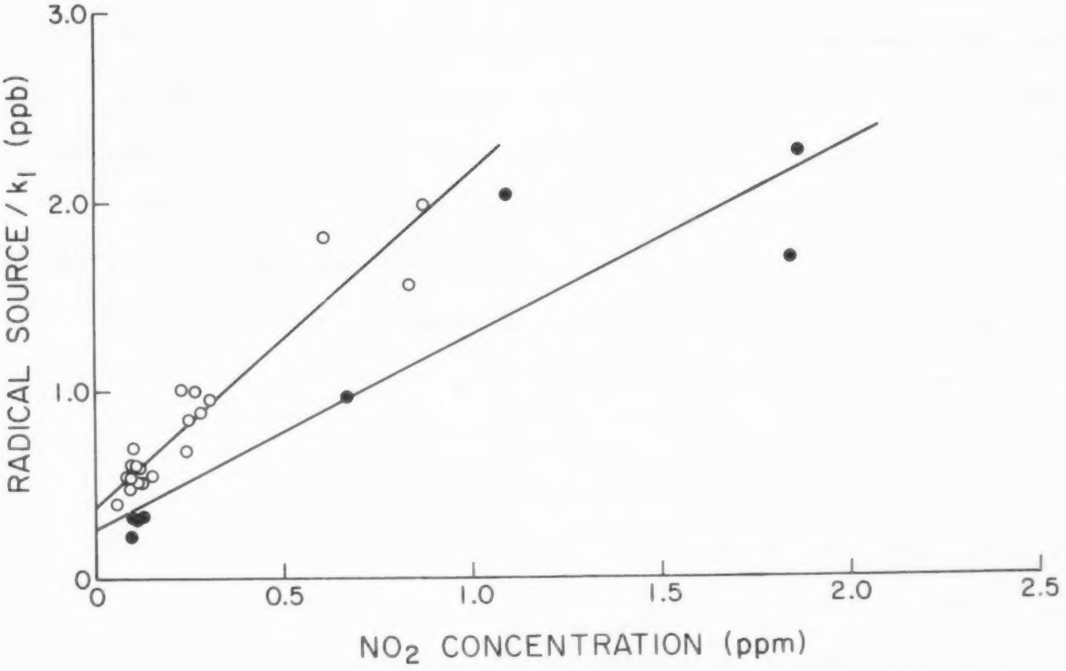

Figure 10-4. Plot of (radical source/k_1) against the average NO_2 concentration for t > 60 min in evacuable chamber irradiations at 303°K; ● - ~0% RH; o - ~50% RH.

organic-NO_x-air irradiations. (The standard procedure between runs in this chamber is to evacuate the chamber overnight, but at ambient temperature [Pitts et al., 1979].) Thus, although "dirty-chamber" effects may contribute somewhat to this radical source under some conditions, the data do not support the assertion that contamination is the only contributor.

Table 10-1 illustrates the dependence of the radical flux on the chamber volume and material (at low humidity and T = ~303°K). Since the radical fluxes were shown (at least for the evacuable and ~6400-liter indoor Teflon chambers) to be proportional to light intensity, the values shown in the table are normalized by dividing the radical fluxes by k_1 (the NO_2 photodissociation rate constants) for a more direct interchamber comparison. The data shown in Table 10-1 were taken from typical runs when the chamber was new or newly conditioned (for the 100-, 6400-, and 40,000-liter Teflon chambers) or when the chamber was in "standard" condition (i.e., following an overnight, ambient-temperature evacuation for the evacuable chamber). The normalized radical flux appears to be somewhat higher in the evacuable chamber than in the Teflon chamber of similar volume; to what extent this higher flux is related to the different type of surfaces involved, or to contamination of the evacuable chamber, remains unclear. For the Teflon chambers, the radical flux decreased significantly when the volume was increased from ~100 liters to ~6400 liters, but surprisingly did not decrease further (within experimental variability) when the volume was further increased to ~40,000 liters. This observation suggests, though it certainly does not prove, that at least some component of this radical source may be independent of the chamber, and thus may operate in the open atmosphere.

TABLE 10-1. DEPENDENCE OF RADICAL SOURCE ON CHAMBER*

Chamber	Approximate Volume (L)	k_1 (min^{-1})	[OH] (10^6 cm^{-3})	Radical Source/k_1 (ppb)
Teflon Bag No. 4	100	0.27	4.3 ± 0.6	1.0
Teflon Bag No. 5	100	0.27	1.4 ± 0.1	0.3
Teflon Bag No. 6	100	0.27	2.1 ± 0.8	0.5
Evacuable	5800	0.49	2.4 ± 0.4	0.3
Indoor Teflon	6000	0.45	0.88 ± 0.4	0.1
Outdoor Teflon	40000	~0.3	0.5 ± 0.4	0.1

*Initial [NO] ≅ 0.4 ppm, $[NO_2]$ ≅ 0.1 ppm; RH < 10%; T = 303°K to 308°K.

Additional indications that the radical flux may not be entirely heterogeneous in nature comes from results of evacuable-chamber experiments in which the NO_2 concentrations were suddenly increased in the middle of the run either by injecting NO_2 directly, or by injecting sufficient O_3 to convert some (though not all) of the NO to NO_2. Figure 10-5 gives the results of two such experiments (initial NO ≅ 0.4, NO_2 = 0.1, T = 303°K, ~50% RH). The sudden increases in $[NO_2]$ can be seen to cause no detectable change in the OH radical levels as measured by the decay rates of the tracers, despite the fact that NO_2 is the major radical sink in this system. The slight increase in the propene-consumption rate by reaction of propene with O_3 or $O(^3P)$, which becomes more important as $[NO_2]$ and the $[NO_2]:[NO]$ ratio are increased is much too small to account for this observation. This result is consistent with the

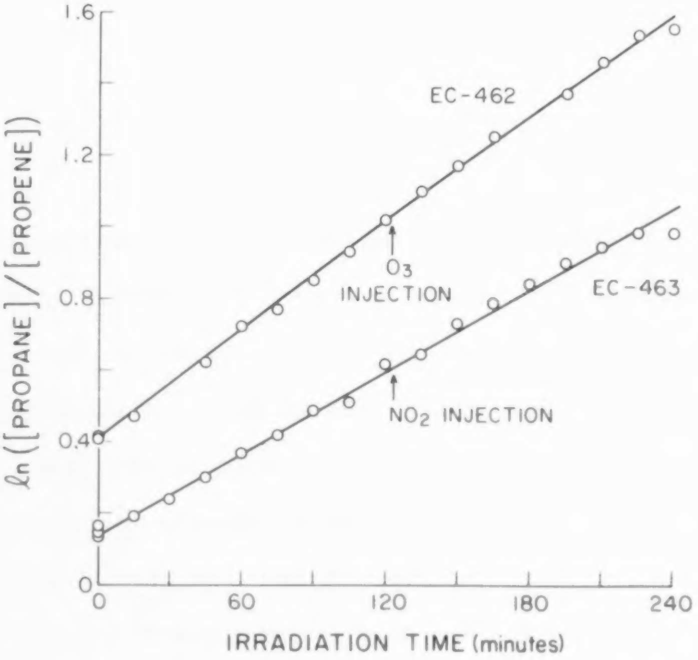

Figure 10-5. Plots of ln ([propane]/[propene]) against irradiation time for evacuable chamber run in which O_3 or NO_2 was injected during the run.

fact that the radical flux increased with $[NO_2]$, but that the sudden increase in $[NO_2]$ does not cause even a temporary suppression of the radical levels is surprising. This lack of radical suppression suggests that the process in which the radical precursor is formed from NO_2 is quite rapid, more rapid than one might reasonably expect for a heterogeneous reaction is a 5800-liter chamber.

EFFECT OF AN NO_2-DEPENDENT RADICAL SOURCE ON EKMA PREDICTIONS

To obtain an indication of the uncertainty introduced into EKMA predictions by uncertainties related to the chamber radical source, one may find it useful to determine how EKMA predictions would be affected if the unknown, NO_2-dependent radical source were assumed to operate in the atmosphere. Such a determination would also show how EKMA predictions could change if such a radical source were found to actually operate in the atmosphere. Further, it would give an indication of how predictions of models validated against chamber data, but ignoring the chamber radical source, would differ from those validated with this effect taken into account, since the former models would require some artificial "internal" radical sources in the kinetic mechanism to compensate for their deficiency in representing the chamber radical source in chamber simulations. Note, for instance, that the original Dodge mechanism (Dodge, 1977) and the various Carbon Bond mechanisms (Whitten et al., 1979; Whitten et al., 1980; Killus and Whitten, 1981), which are most frequently employed or proposed for use in EKMA models (EPA, 1977; Dimitriades, 1977; Dodge, 1977; Bilger, 1978; Carter et al., 1982; Hov and

Derwent, In press; Jeffries, 1981; Killus and Whitten, 1981), all fall into this category. Thus, these models may be significantly overpredicting radical levels when applied to the open atmosphere.

Calculation Method and Kinetic Mechanism Employed

The kinetic mechanism and HC representation employed in all calculations reported here was the SAPRC propene-n-butane-formaldehyde model, which was validated (Carter et al., 1982) against the SAPRC "surrogate" HC-NO_x-air glass smog chamber data base (Pitts et al., 1976). The model was validated assuming a continuous chamber radical source that was consistent with results of the NO_x-air irradiations described above. The kinetic mechanism, the HC representation, and the chamber validation have been described elsewhere (Carter et al., 1982). The mechanism was recently updated in several minor details to be consistent with more recent basic laboratory studies and mechanistic interpretations as described by Atkinson and Lloyd (1980), but these changes had only minor effects on its O_3 predictions.

For the purposes of these calculations, the possibility of including an atmospheric, NO_2-dependent radical source was provided by replacing reaction 1 (NO_2 photolysis) with the following:

$$NO_2 + h\nu \xrightarrow{k_1} NO + O(^3P) + \alpha\, OH, \qquad \text{(Reaction 1')}$$

where $k_1' = k_1$ and α was varied from zero (no radical source) to 10^{-3}. Although reaction 1′ has no physical meaning, it is a convenient formalism to relate the radical flux to k_1 and $[NO_2]$ for computational purposes. The type of dependence of the radical source on $[NO_2]$ implied by reaction 1′ (linear with a zero intercept) is not strictly consistent with our smog chamber data (see Figure 10-4), but it is a useful enough approximation for comparative purposes. The value of $\alpha = 10^{-3}$ corresponds roughly to the radical fluxes observed in our larger environmental chambers (Carter et al., In press).

The conditions employed for the EKMA simulations discussed here are based on those used for the standard (or default OZIPP [Whitten and Hogo, 1978]) isopleth calculations, except for the kinetic mechanism and HC representation (Carter et al., 1982). Full pollutant loading at 7:00 a.m. local standard time (LST) was assumed, and the simulation was terminated at 6:00 p.m. LST. A constant dilution rate of 3% h^{-1} was used. The initial $NO:NO_2$ ratio was assumed to be 3, and all calculations were done for a latitude of 34.1°N and a solar declination of 23.5°, which are appropriate for Los Angeles in the summer. Initial HONO was assumed to be negligible in these calculations. Photolysis rates were calculated using the actinic irradiances as a function of zenith angle derived by Peterson (1976) using his "best estimate" surface albedos. These conditions may not be the most realistic, but they have been used in previous sensitivity studies (Dodge, 1977; Carter et al., 1982), and are useful for comparative purposes.

Results of Calculations

Figure 10-6 compares isopleths for O_3 = 0.12 and 0.3 ppm calculated with and without the NO_x-dependent radical source. This inclusion of this radical source had no singificant effect at low HC:NO_x ratios, but significantly less inhibition by NO_x is predicted at high HC:NO_x ratios if the NO_x-dependent radical source is assumed. This is reasonable, since at high HC:NO_x ratios, O_3 formation is limited by NO_x availability, and increasing the radical initiation makes the O_3 maximum occur earlier without strongly affecting the O_3 yield. On the other hand, at high HC:NO_x ratios, O_3 formation is limited by the length of the day, and thus if more radical initiation is occurring, more O_3 can be formed while light is available.

To determine whether the predicted changes in the isopleths caused by assuming an NO_2-dependent radical source significantly impact the predictions for HC control strategies, these isopleths were analyzed using the standard EPA-recommended "relative" isopleth analysis technique (EPA, 1977; Dimitriades, 1977). The technique was used to determine the amount of HC control required to reduce O_3 from 0.3 to 0.12 ppm, assuming that the NO_x levels remain the same. The predictions of this technique are sensitive to the NMHC:NO_x ratio assumed, and since this ratio is highly uncertain even for the Los Angeles basin (CIT, 1980), the required HC controls were calculated for a range of HC:NO_x ratios from 6 to 12. The results are shown in Figure 10-7. Regardless of the HC:NO_x ratio assumed, the percentage of HC control predicted to be required is greater if an NO_2-dependent radical source is

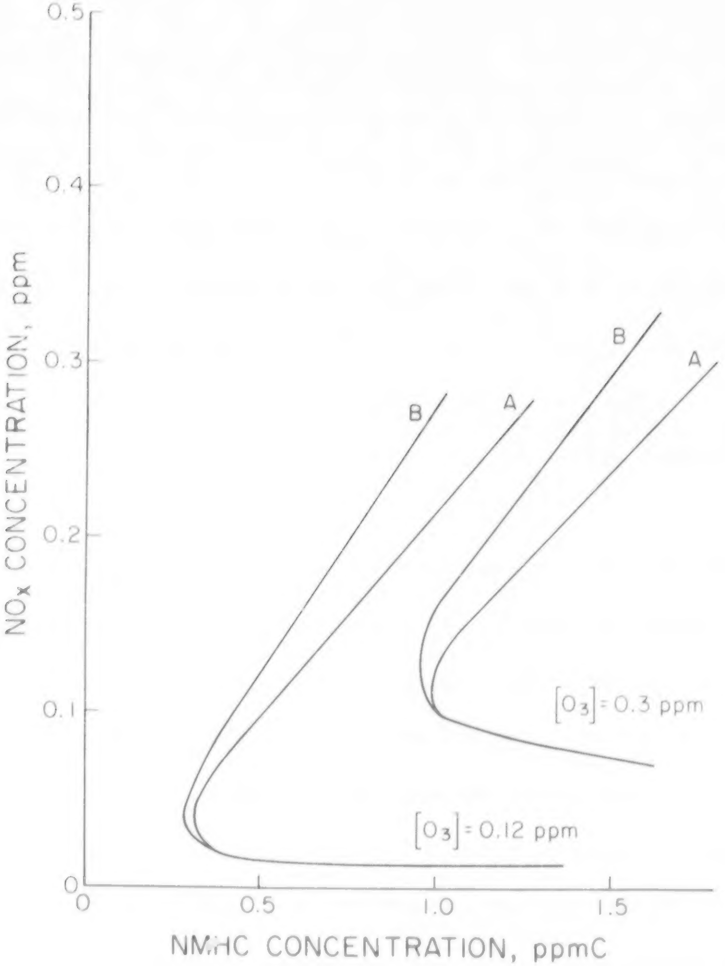

Figure 10-6. Calculated O_3 isopleths at 0.12 ppm and 0.3 ppm. A - no NO_2-dependent radical sources; B - radical input rate = $10^{-3}\ k_1[NO_2]$.

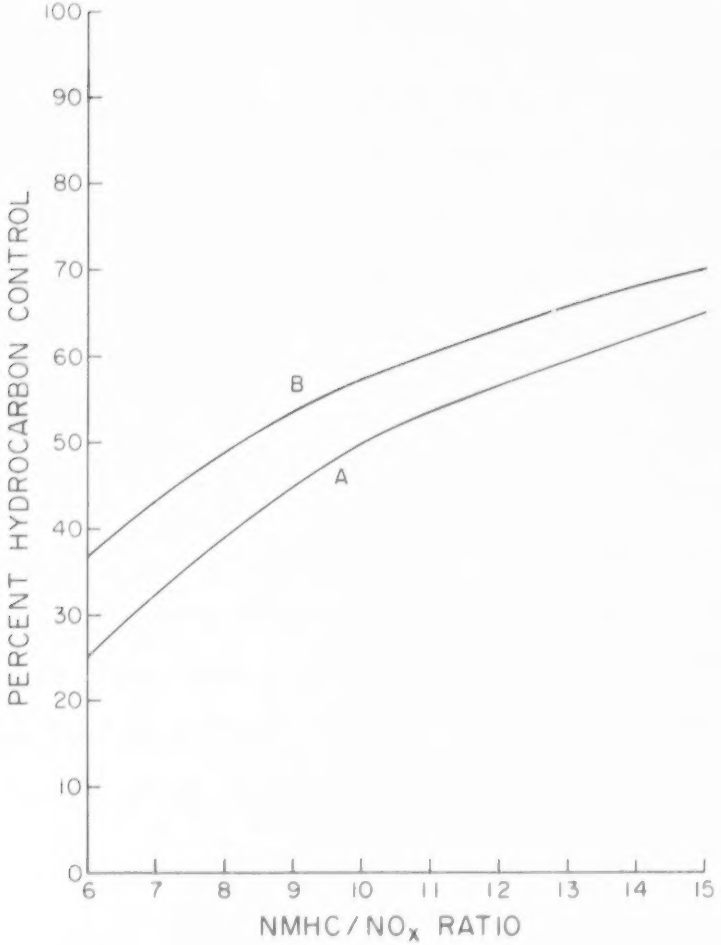

Figure 10-7. Predicted present HC control required to reduce O_3 from 0.3 ppm to 0.12 ppm for a range of HC:NO_x ratios. A - no NO_2-dependent radical source is used; B - radical input rate = $10^{-3}\ k_1[NO_2]$.

assumed. In addition, the discrepancy between the models increases as the NMHC:NO_x ratio is decreased.

EFFECT OF INITIAL HONO ON EKMA PREDICTIONS

A less speculative source of radicals in ambient air is HONO, a powerful photoinitiator (Stockwell and Calvert, 1978), which has recently been observed at levels of up to ~8 ppb in a Los Angeles source area (Harris et al., 1982). Although the mechanism of formation of HONO in the atmosphere is unknown, HONO was observed to increase slowly throughout the night. Nitrous acid may be emitted along with NO_x, or it may be formed homogeneously or heterogeneously from NO_x previously emitted. Since the mode of HONO formation is unknown, and direct ambient HONO measurements in urban source areas are extremely limited, the amount of initial HONO appropriate for use in city-specific EKMA calculations if unceratin. To determine the nature and magnitude of the impact of this uncertainty on EKMA predictions, and to compare this to the effect of the uncertainties related to the NO_2-dependent radical source, EKMA calculations including 5 ppb and 10 ppb initial HONO (independent of NO_x) were compared with those assuming no initial HONO.

Except as noted, the kinetic mechanism, HC representation and conditions, and input data assumed were the same as those employed in the calculations examining the effect of the NO_2-dependent radical source discussed above. These calculations were performed prior to our updating the mechanism based on the review of Atkinson and Lloyd, 1980); but, as mentioned above, these changes were minor, and thus the mechanism was essentially the same. In these calculations, no NO_2-dependent radical source was assumed ($\alpha = 0$). In those calculations where initial HONO was included, it was incorporated as a component of the initial NO_x because it rapidly forms NO upon photolysis. Thus, for example, a calculation assuming 0.1 ppm initial NO_x with 10 ppb initial HONO used initial $NO + NO_2 = 90$ ppb.

Figure 10-8 compares isopleths for $[O_3] = 0.12$ ppm and 0.3 ppm calculated using 0, 5, and 10 ppb initial HONO. The effect on the isopleths of assuming initial HONO is similar to the effect of assuming an NO_2-dependent continuous radical source -- the O_3 yeilds are unaffected at low NO_x:HC ratios, but greater O_3 formation is predicted at high NO_x:HC ratios. The main difference between assuming initial HONO and assuming an NO_2-dependent radical source is that in the former case, the isopleth lines at high NO_x are parallel to those of the control calculations, rather than diverging (compare Figure 10-8 with Figure 10-6). This difference can be attributed to the fact that in the initial HONO calculations the amount of HONO added (5 ppb or 10 ppb) was the same at all NO_x levels, and thus the amount of excess initiation in the calculations was independent of NO_x. In the calculations with the NO_2-dependent radical source, the excess initiation increased with NO_x. If calculations were performed in which the initial HONO was assumed to increase with initial NO_x (as is perhaps reasonable to expect for ambient air conditions), then the isopleths would diverge as observed when the NO_2-dependent radical source is assumed. Thus the effects of these two

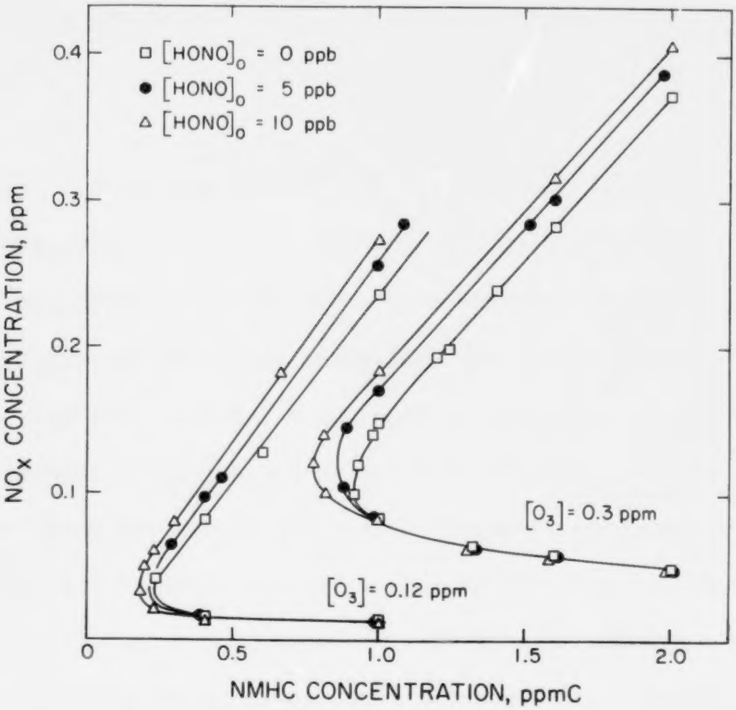

Figure 10-8. Calculated O_3 isopleths at 0.12 ppm and 0.3 ppm for cases where HONO = 0, 5, and 10 ppb.

different types of NO_x-dependent radical sources on the isopleths can be considered quite similar.

Figure 10-9 shows the percent HC control required to reduce O_3 from 0.3 ppm to 0.12 ppm at constant NO_x, as a function of NMHC:NO_x ratio, calculated using the "relative" isopleth analysis techniques (EPA, 1977; Dimitriades, 1977), and the HONO = 0, 5, and 10 ppb isopleths. Consistent with the results shown in Figure 10-7, increasing radical initiation increases the predicted amount of HC control required. (The increased control predicted as a result of increased initiation is also consistent with the effect of increasing initiation by increasing the aldehyde content in the representation of the reactive organics [Carter et al., 1982]). The results of these calculations indicated that a ± 5 ppb uncertainty of initial HONO assumed in EKMA calculations can cause an uncertainty of greater than ~ ± 5% in predictions of required HC control, regardless of the NMHC:NO_x ratio used.

CONCLUSIONS

The amount of radical initiation in EKMA model calculations can be increased either by changing aspects of the kinetic mechanism related to rates of radical production or by increasing the levels of radical initiation assumed to be present. Both of these increases tend to affect calculated O_3 isopleths by decreasing the efficiency of NO_x in suppressing O_3 at high NO_x:HC ratios, while leaving the isopleths unaffected at low NO_x:HC ratios. We find that the "relative" technique for analyzing isopleths can be quite sensitive

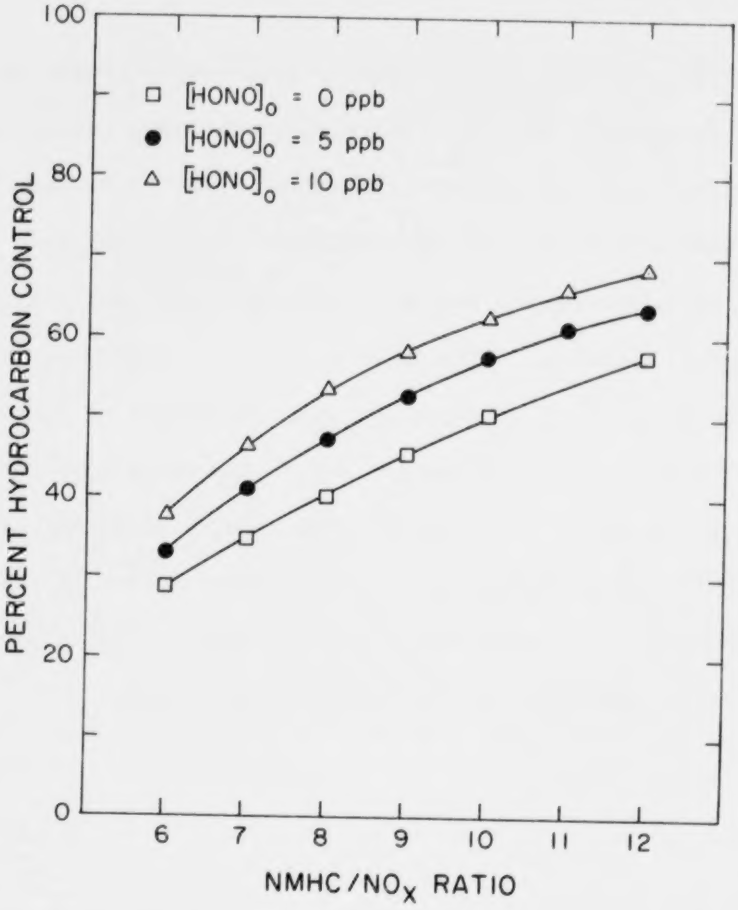

Figure 10-9. Predicted percent HC control required to reduce O_3 from 0.3 ppm to 0.12 ppm for a range of HC:NO_x ratios in cases where HONO = 0, 5, and 10 ppb.

to this type of change in the isopleths, particularly when it is used to predict the percent HC controls required to achieve a specified O_3 reduction without controlling NO_x. This sensitivity of the "relative" isopleth analysis technique contrasts with the results of a previous study conducted by Dodge (1977), in which this type of analysis was found to be fairly insensitive to other aspects of the model, such as HC reactivity (i.e., the propene:n-butane ratio), dilution, or light intensity. However, our results are consistent with results of other sensitivity studies (Carter et al., 1978; Hov and Derwent, In press; Jeffries, 1981) in which EKMA predictions were found to be significantly affected when different kinetic mechanisms were employed.

The sensitivity of EKMA predictions to the kinetic mechanism employed means that it is essential to utilize a valid mechanism in EKMA models. Thus, for example, the continued use of the original Dodge mechanism (Dodge, 1977) cannot be supported, since that mechanism, originally developed in 1974-75 (Durbin et al., 1975) is now known to be incorrect in a number of its details (Carter et al., 1982; Hov and Derwent, In press; Pitts et al., 1980) and to give significantly different predictions than more current models (Carter et al., 1982; Hov and Derwent, In press; Jeffries, 1981; Pitts et al., 1980). Two necessary conditions for a mechanism to be valid are that it be consistent with the results of basic kinetic and mechanistic studies and that it be able to simulate adequately results of smog chamber experiments, while properly taking chamber effects into account. Until recently, validating aspects of the mechanisms related to radical initiation has been difficult because of excess radical sources observed in chamber experiments and disagreement among modelers on how best to handle them (Carter et al., 1979; Hendry et al., 1978; Falls and Seinfeld, 1978; Whitten et al., 1979; Whitten et al., 1980; Harris et al., 1982; Killus and Whitten, 1981). However, the chamber characterization experiments discussed in this paper and in more detail elsewhere (Carter et al., In press) have shown that continuous radical source(s) do exist and provide a method by which their magnitude can be readily measured. Thus, the radical source no longer must be treated as an adjustable parameter when models are validated against smog chamber data; measured values from separate characterization experiments can be used. Clearly, mechanisms that have not been validated with the chamber radical source properly taken into account should not be used in EKMA and other airshed models, and in particular should not be recommended for use in control strategy planning.

However, even for properly validated kinetic mechanisms, there remain uncertainties in EKMA calculations related to radical initiation. For example, it is not presently known to what extent the continuous NO_2-dependent chamber radical source is important in the open atmosphere. The levels of initial HONO appropriate for use in city-specific airshed simulations are also unknown, except perhaps for Los Angeles (Harris et al., 1982). Calculations performed by varying these parameters within their range of uncertainty show that these factors have non-negligible impacts on calculated O_3 isopleths and control-strategy predictions. Clearly, additional research is required to establish characteristic atmospheric levels of known radical initiators such as HONO and aldehydes more clearly, and to determine whether there are other significant atmospheric radical sources that are not included in current models.

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COMMENTS

Herbert McKee

I wanted to make a few comments on the ways in which the Empirical Kinetic Modeling Approach (EKMA) and other mathematical models are used in the real world. I realize this is a technical meeting, and I certainly don't intend to take up any time with our administrative and legal problems at the state and local program level. However, program administrators in air pollution control have some serious problems in attempting to meet the O_3 standard.

The reason I am bringing these problems up is that their solutions can only be found at the technical level, that is, at the level where these models are developed and their limits determined and described.

Our past history in this area is not encouraging. In 1971, the U.S. Environmental Protection Agency (EPA) decided everyone had to use Appendix J, and they absolutely guaranteed that everyone would attain the oxygen standard by 1975. The only trouble with that was that in Houston, Appendix J would have required 110% reduction in hydrocarbon (HC) emissions. When this was pointed out as theoretically and practically impossible, EPA reverted to proportional rollback, and that did not work either. So, then they came up with modified rollback.

The end result of all this, modeling aside, was that massive monetary expenditures were made for HC controls. Dr. Basil Dimitriades and Dr. John Trijonis disagree on the amount of reduction. I can assure you there have been some very substantial expenditures for control equipment; I have seen the hardware and I have watched it operate. I think some of Dr. Trijonis's figures are based on comparing emissions inventories at two different times that were assembled by different techniques and are not comparable.

Nevertheless, the easy and obvious things to control HC's have been done. Further reductions in HC emissions comparable to what the control measures that have already been implemented have accomplished are not possible. We have done the easy and the obvious. Any further control efforts involve the smaller subtle sources that are harder to find and control. So, now we are trying to use EKMA to determine how much of a reduction is required.

Some of the discussions today and some of the things I have heard over the last 2 or 3 years about EKMA remind me of the young engineer who was told to derive a very quick and very approximate estimate of the capacity of a tank sitting out on a tank farm. He went out and paced around it so many paces and assumed he walked 3 ft at a step, and reached up on the side and figured it was about so much higher than he could reach. Then he went back in with that beginning data and divided by pi on his calculator to 14 decimal places and reported the capacity of the tank as 1,751,489.5 gal.

Now, obviously, his input data did not justify the accuracy which he tried to attach to the results. I think the same thing is happening here to some extent. The State Implementation Plan (SIP) requirements, the Clean Air Act, and EPA regulations presume that control requirements will be established that will exactly meet the standard by July 1, 1987, and that after that, with the exception of 3 exceedances every 3 years, the highest ozone (O_3) anyone will record is going to be 11.999 ppm for maximum day for each year. I think our experience with reducing HC's but failing to reduce O_3 measurably over the last 10 years in Houston indicates there is no assurance this is going to work out that way.

Here are a few reasons I think apply. First of all, there has been some discussion about emissions inventories. Emissions inventories can, or usually, include only what is expected to be emitted into the atmosphere under steady-state conditions. I am talking now about stationary sources, industrial sources which can, by and large, control our Houston situation--steady-state conditions at or near design capacity.

In reality, operating rates vary. A lot of refineries are now running at 70% capacity, and that makes more than a 30% difference in the emissions compared to running at 100% capacity. Emissions during start-up and shut-down differ drastically from what they are both qualitatively and quantitatively at steady state. In addition, fugitive emissions are either not included in emissions inventories or are included only by some very rough approximating techniques whose accuracy is not known. Over the past 3 or 4 years, I have heard estimates of fugitive emissions expressed as a percentage of process emissions, ranging from 10% to 200%. So somewhere in that range there are fugitive emissions from leaking valves, from pipe flanges, pump packings, accidental spills, and sources of that nature. There are thousands of them in a typical plant.

Temporary malfunctions are also not in the inventory. No one compiling an emissions inventory can predict, for example, when a large ethylene plant might lose electric power to a compressor and possibly lose as much as 1,000,000 lbs/h of feed stock for several hours or something like that. Those emissions are not in the emissions inventory.

However, we are beginning to accumulate some evidence, although circumstantial, that some of the O_3 episodes in Houston may be related to accidents of this type. The O_3 episodes occur in the areas immediately downwind of whatever plant experiences a major emergency a few hours after the emergency occurs.

Another factor is that HC reactivity varies widely. The modeling efforts in the past have treated everything alike in terms of tons of nonmethane HC's (NMHC's). I am glad to see we are getting away from that in terms of the description of chemical reaction mechanisms here. But, obviously, refinery, chemical plant, and automobile exhaust emissions vary widely in their reactivity, pound per pound.

Ambient monitoring is uncertain for some of the same reasons, especially for NMHC's. When the NMHC standard was first promulgated, the Beckman instrument was the only one available. Beckman has gone out of business, and about every year someone tells me something different concerning whether or not it is now possible to measure NMHC's in the ambient atmosphere with any accuracy or precision. I get a different answer every time I ask someone who is presumably an expert in the field.

Monitoring of NO_x was not very reliable until recently, in part because there was no standard for NO. There was only a standard for NO_2, and the Jacobs method for measuring that had to be abandoned. In addition, the chemiluminescence measurement technique was developed too rapidly. The first instruments we bought after that method was selected proved to be unstable and unreliable. We are still trying to replace some of those with more reliable updated instruments. Our NO_x data are not very good, either, partly for that reason.

Chemical reaction mechanisms may vary as has been discussed here in great detail. Instead of trying to select the Dodge, the Carbon Bond II, or whatever other mechanism, it is conceivable that a different reaction mechanism might be needed for the area downwind of one end of the Houston Ship Channel, for example. The emissions in this area are largely from refineries. Perhaps a different reaction mechanism is needed for another portion of the Ship Channel downwind from the petrochemical operations. A different mechanism might be needed for the feed stock area with its highly reactive butylenes and those type materials. The time of the reaction varies, depending on the meteorological conditions and what the materials are, olefins, aromatics, or whatever.

Our O_3 episodes are extremely variable, both in time and in space. We have seen high O_3 levels over most of the city simultaneously, but more often we will see high O_3 at the monitoring station. Other monitoring stations will be much lower. I have even seen two monitoring stations 6 to 8 mi apart, one of which measured over 0.2 ppm O_3 and the other one at practically natural background, 0.04 ppm, 0.05 ppm, or some O_3 level like that.

Obviously, some of the precursor sources in some portion of the city are involved in that one high reading, but certainly other precursors in the emissions inventory on a county-side basis can have nothing to do with what we measure.

In Houston, O_3 occurs without the simultaneous occurrence of high irritation and photochemical vegetation damage that has occurred in Los Angeles at comparable O_3 levels. And, O_3 can occur with or without haze. I have seen conditions of 0.2 ppm O_3 with a visibility of 2.5 or 3 mi. I have also seen 0.2 ppm O_3 with a visibility of 100 mi if you get up high enough in the air to see 100 mi to the horizon.

Another factor is transport. A lot of days we can account for our O_3 based on our own precursors. Other days it looks like half or occasionally even more than half of the O_3 we measure over Houston results from precursors coming into the Houston area from somewhere 50 to 100 mi away. This is based on measurements of the upwind area inside of the city.

I could give lots of other reasons, but, in short, the O_3 episodes that occur in Houston, and I suspect in some other cities where you do not have a mountain barrier to create a basin effect, are too variable for any single modeling method to measure accurately, even most of the time.

The principle of modeling is that you are looking at a series of events which qualitatively are identical or at least very similar. The purpose of modeling is to describe accurately the quantitative differences from one time to another. I think we are dealing with a phenomenon here which qualitatively is different from one episode to the next, so obviously, the quantitative differences described by modeling cannot be very accurately described as a basis for predictions unless you account for the qualitative differences that caused the episode in the first place.

Can these problems be rectified? I do not think so, at least not all of them. Certainly our knowledge of chemical reaction mechanisms will be approved, and I am glad to see the knowledge that is being gained in that area. But, no emissions inventory will ever include an accurate estimate of the emergency emissions from upset manufacturing processes or emergency malfunctions.

So, I think the best approach, at least from the standpoint of the local control agency, is to change the monitoring approach a little. This is critical to all we are trying to do and to all the use that is going to be made of whatever models are ultimately developed.

At the present time, modeling is used as practically the sole determinant to find out what control strategy is required and how far it has to go. Sometimes this is carried out to several decimal places, like the engineer that I described earlier that used pi to 14 decimal places.

We got into a big argument years ago over whether certain control measures in Houston that were proposed would reduce HC emissions by 0.1% or by 0.2%. If anyone can tell me how to measure that difference in an O_3-monitoring instrument anywhere in the city of Houston, I would like to hear it. This kind of argument certainly misses the main point, both of monitoring and of trying to control O_3 in the first place.

Monitoring is not an automatic cure-all. It is not reasonable to plug numbers into a computer and use the results that the computer feeds back automatically. That is where I think the major fallacy is--in the way monitoring is being used now--because with that approach, no judgment or common sense is involved.

Modeling can be very useful, but to be useful I think modeling should be used as an aid in exercising judgment and common sense, not as a substitute for them.

That philosophical point, I think, has a bearing on what you the technical experts in developing mathematical models are going to do or can do. Present efforts seem to be aimed at eliminating all the sources of air in these models so that you can develop some perfect model that is going to be accurate, maybe even to 14 decimal places, and everybody can use it. We can use it in Houston, our counterparts can use it in Philadelphia or anywhere else they see the O_3 problem; they can use this mathematical model by plugging in the input data and the computer will tell them that they need to reduce HC's by 30.78% or whatever the answer is.

I think this is impossible. If models are to be most useful for their ultimate application of trying to improve air quality, it would be more helpful if the experts could define the advantages and the limitations of the various models available and of the various chemical reaction mechanisms that might be used in these models, and, thus, make it possible to evaluate the O_3 problems of a particular locality.

I do not think an approach will ever work where every urban area that has to control O_3 uses the same model, or even different variations of the same model.

If the advantages and limitations of a series of models are described, we can pick out certain ones that seem to be applicable to our problem. As I said before, we might use one for one end of the Houston Ship Channel and a different one for the other end of the Channel, and still a different one when the wind blows.

Or, one might use a different one when there is evidence that part of our O_3 precursors are coming in from Texas City or Beaumont or somewhere else. Our counterparts in Philadelphia and St. Louis or wherever else might pick different models designed to fit their particular local circumstances to control their O_3 problems.

If this could be done, I think models would be most helpful as an aid in exercising the judgment and common sense that has to go into control strategies. Anyhow, this would make it easier and much more practical for the control agencies to get away from what appears to be the present approach of using models as a substitute for judgment and not as an aid to it.

WORKSHOP COMMENTARY

ESCHENROEDER: Dr. Jeffries, what kind of sample automobiles do you intend to use? Will they be new versus in-use or aged ones?

JEFFRIES: We've looked at about 10 to 12 vehicles that Ron Bradow has a long history on.

They have a series of vehicles that they've countinued testing over a long time, so we have a range from which to choose.

My initial tendency would be to take one or two vehicles and focus on those until we can understand the behavior and performance of those.

There are some problems with measuring HC emissions from the new catalyst-equipped vehicles. The HC emissions you do get only occur in the first 506 sec of the federal test. After that, the catalyst is hot and there aren't really emissions. So you have to take a sample from the tailpipe during that period, because after that you don't get very much.

The mixture will depend upon how well we can get everything else working. If it proves to be simple, yes, we can take samples from a lot of them and we can cover a wide range.

Some of the cars have been misfueled. That is, they have had leaded gas put into the catalyst system, and they come out way up on the top of the diagram. Of course, we would like to look at one of those versus one that's brand new.

The newest Buick available, a 1981 Buick, with double filtering on the emissions has an extremely low HC emission and extremely low evaporative emission.

It doesn't look like a very productive vehicle for our purposes. If all the cars on the road were like that, we wouldn't have any trouble.

So, a series of cars is available that we can examine. We just haven't decided exactly what we'll look at and at how many, because it depends upon how difficult it is to do.

CARTER: Do you have any diesels?

JEFFRIES: Yes, some diesels. I don't know that we have plans at this stage to look at those. That may be for a second year study.

UNIDENTIFIED SPEAKER: There are gas-based organics on those that are really in question, though--

JEFFRIES: Ron Bradow had to generate 2.5 kg of diesel particulate for it, so he's got plenty of diesels and so forth.

LLOYD: Do you have any composition data on the evaporative compared to the tailpipe?

JEFFRIES: Yes. Ron Bradow has a fair amount of data that he's obtained from a wide range of vehicles, for approximately 54 compounds I think. I've done some analyses and looked at the relative groupings and behavior. Winter versus summer gasoline makes a substantial difference in emissions because the blend is changed to raise and lower the vapor pressure on it, which greatly affects the evaporative emissions.

It looks like for all the newer vehicles, evaporative emissions constitute at least 50% of all emissions. However, the question arises of how to sample evaporative emissions in this case. Our chamber's big, but we don't want to park an automobile in it. So, it's a question of I can't take the whole shed volume.

KELLY: What about a canister?

JEFFRIES: That's an option we're considering. We've discussed getting an actual canister, using whole gasoline, and going through an equivalent. The problem is that it's a process; the car starts out hot and as it cools down you get very strange emissions behavior.

LLOYD: Are you going to try different brands of gasoline?

JEFFRIES: I think in the beginning we'll freeze gasoline. Then, as we go, we'll see how well things move. All kinds of options are open to us.

Initially, we would like to have enough of a data base to exercise the critical factors in the models that are being popped up right now and see how well they track those kinds of behavior.

But many, many issues are open. We will just have to see how well things go.

McKEE: You mentioned that some of the vehicles had been misfueled. Were they misfueled over a period of time or just once or twice?

JEFFRIES: I think this one had been so misfueled that the catalyst had burned out.

McKEE: Okay. The reason I asked is that if you only run one or two tankfuls of leaded gas and then return to unleaded gas, the catalyst will recover. I've confirmed this on my own car as part of an experimental program we did.

JEFFRIES: Sure, we heard about the Houston program using police cars.

McKEE: That was a different experiment. In the experiment of the city vehicles that I drove--

JEFFRIES: The emissions on the misfueled car, a Ford Mustang, were factors of 5 or higher than on the other cars.

McKEE: In my case, I ran one or two tankfuls of leaded gas and then returned to unleaded gas. In about three or four more tankfuls of unleaded gas, the emissions had returned to the prior level when measured as THC's by infrared.

Now I don't know whether the composition of the HC had changed, but to an I&M type screening instrument, the emissions were the same, essentially the same.

JEFFRIES: I think the issue of misfueling may be something critical we should look into pretty early in the program. Considering the California experience in the last gasoline shortage when small adapters went on sale everywhere, I think we should find what the effects might be.

TRIJONIS: Concerning the aging of the evaporative control systems, the Aerosol Research Branch of EPA discovered a lot of deterioration in those, so your mix can change with the vehicle.

JEFFRIES: Yes, but this is a follow-up to another program that we are now conducting in which we are looking at a data base for reactivity testing for photochemical models. We have systematic variation in composition and complexity of the mix over a wide range. This is on both sides of the chamber at the same time. We've already produced 30 or 40 dual runs in which the compositions differed and we've substituted toluene versus xylene.

So, there is a preceding simple data base, if you want to think about it that way. That data base can exercise the models up to the point where if it can track all of those changes you then give it the automobile exhaust with its complexity and see if it can also track those changes.

ROMANOVSKY: How do you propose to deal with the question of the dirty chamber and leaking chamber?

JEFFRIES: If I'm at levels of 6 ppmC and 0.6 ppm NO_x, I don't think I have to worry about dirty chambers.

We will probably be at a high enough level, and we've got plenty of data on our chambers, that the modelers won't have any troubles dealing with our chamber. We've got 153 m^3 volume in each side, and we've done a whole range of systematic tests to examine dirty chamber effects.

We don't expect to do experiments at this point at low levels of HC and NO_x. We may make low levels of O_3, but that's because of the HC:NO_x ratio problem.

ROMANOVSKY: Dr. Bufalini, I believe, made the comment earlier that evidently it is extremely important to have the data at that point. As far as Los Angeles is concerned, we're probably 50 years away from worrying about getting under point--

JEFFRIES: In my presentation this afternoon, I will discuss the problems associated with mechanisms and model predictions and experimental data as you decrease the HC concentration and drop to lower and lower O_3 levels. So you will see some impact of what happens this afternoon.

ROMANOVSKY: I have a short question for Dr. Lloyd. Did you get a chance to look at and compare the O_3 which you generated in the chamber with the O_3 measured by the district monitoring station downwind along the trajectory of the air mass?

Also, did you compare temperatures inside and outside the chamber?

LLOYD: We are gathering data to do that. We have not gathered all the data together yet, but that is part of the program.

Concerning temperature effects, a couple of days got pretty warm. In general, the fall was cooler than expected, consistent with the fact that the O_3 wasn't as high as normal. Thus, that didn't turn out to be the problem that we expected. Some days were actually pretty cool.

ROMANOVSKY: It's a concern I've had that the differences in temperature might make that approach somewhat defective.

LLOYD: On a couple of the days, the temperature was really thought to be too high. But most days it was cool; it felt like winter on some of those days.

FINAL DISCUSSION

DIMITRIADES: On the subject of chemical mechanisms, the first presentation you heard was by Gary Whitten. He described the various mechanisms now in existence, and pointed out some of the differences and some of the advantages and disadvantages of the various mechanisms. You then heard Harvey Jeffries talk about comparisons of the various mechanisms against a set of data. Finally, Bill Carter made a case for consideration of chamber reactions.

Several questions have been raised, and I'm sure some of them have been answered. But, some questions remain that I think are important to discuss, or at least to use as a starting point for the discussion.

I guess the first question I would like to raise is: Would it be desireable and appropriate, or necessary, to define a standard set of data and a standard procedure by which you can compare those items? I appreciate the desire of each modeler to define his own mechanism in terms of not only the reaction pathways but also in terms of a set of data that suit his mechanism. But, I wonder if this is right. Should we come up with a standard set of data against which we can compare the mechanisms?

I would like to go back to the question I raised earlier. If we do need a set of data against which to compare or judge mechanisms, should this set of data be smog chamber data, ambient air data, or what? In fact, I'd like to go a bit further, speaking of smog chamber data. Should it be outdoor chamber data or indoor smog chamber data? We want to discuss conceptual advantages and disadvantages as well as the practical ones.

The other question I have is that suppose we do have a mechanism that is perfect in the sense that it describes the mechanisms of some individual organics like propylene, butane, or aldehydes. We want to use this mechanism on the real atmosphere, which consists of a mixture which is undefinable, that is, we don't know what the composition of the ambient organics mixture is. How do we get around this problem? If we don't have the composition of the ambient mix of organics, what good is it to have a perfectly good mechanism for individual organic components? In other words, how do we use this mechanistic knowledge in predicting or making judgments of the real atmosphere?

I think these are some of the questions that I, personally, would like to raise. I don't for a minute suggest that these should be the only ones. But perhaps we can use those as a starting point. So, if you agree, I would like to start with the first question. Do we need a standard set of data; do we need a standard procedure by which we should judge the mechanisms relative to each other, and, of course, with respect to their absolute performance? If we do need such a set of data, do we have it, or if we don't, how do we go about getting it?

KILLUS: I would like to address the question of chemical mechanism use.

Dr. Whitten and I began Carbon Bond mechanisms quite a number of years ago. We are right now, as everyone knows, on Carbon Bond III. From the very outset, we were pretty much like any other kinetic mechanism development group in that the mechanisms we developed were for our use, and when other people tried to use them, they had all the standard problems.

Since that time we have developed something of a methodology for at least trying to let them be used by other users. We generally do not reformulate the mechanisms in a large sense. Carbon Bond III is the third such mechanism, and we do it about once every 3 years. Between those times, we allow ourselves about one reasonable rate constant change such that it can be changed in the airshed model, but we do not reformulate the chemical expressions or the product yields at all.

Contrary to what Dr. Jeffries said, we don't have 30 different versions of the Carbon Bond mechanism for each time. The difficulty we had with Dr. Jeffries was we were sending in computer outputs when we were in the development phase of the Carbon Bond mechanism. During that development we had 30 different sets of rate constants, but we nailed it down pretty carefully right after that.

I would suggest that chemical mechanisms should be documented. One suggested test of a mechanism for someone other than the developers would be whether it has adequate documentation. We have tried to do that, and strongly urge other groups to do it. Then, at least, given a standard set of data on which to prepare mechanisms, one would be able to have others besides the developers use the mechanism against that standard data set.

So, I believe that a standard data set is necessary. I also believe that a standard procedure or procedures of documentation and use are necessary. Those do not exist right now.

DIMITRIADES: What do you mean by documentation?

KILLUS: Well, we have just written what can't be called a manual, but is something that's close to it. It has been given at least in its draft form to several users. Dr. Jeffries sent it to someone in Australia who about 2 days after he received it was able to prepare a smog chamber simulation on a smog chamber that we had never seen before on a HC mix that we had never seen, and, in fact, we still don't know precisely what was done on it. But, the user was reasonably satisfied. He said the mechanism worked pretty well and the documentation was such that he could prepare the simulation without--

DIMITRIADES: I presume that includes getting data as well, rate constants?

KILLUS: Of course. In general, despite what Dr. Whitten said about being able to fix mechanisms when you're allowed to alter the rate constants, if once you've allowed mechanisms to go out into the general user community, certainly that is no longer true. Chemical rate constants should certainly be fixed, and that's really what you're talking about when you say a mechanism.

The differences between a Demerjian mechanism and the Cal Tech mechanism and the ERT mechanism have more to do with rate constants and stoichiometric yields of organics than any other single feature. In fact, I've demonstrated that at least some mechanisms can be made to look very much like other mechanisms if you're allowed to adjust several rate constants.

I took the Cal Tech mechanism about a year and a half ago and prepared an isopleth diagram that was almost identical to a Carbon Bond mechanism isopleth diagram; whereas, as Dr. Jeffries showed you, the original isopleth looks quite different.

DIMITRIADES: To make a judgment on the mechanism, should we have a bunch of experts, who are familiar with the latest kinetic data information, make a judgment of whether those rate constants are right or wrong? Or rather than do that, should we develop this judgment by comparing the mechanistic predictions against those on a second smog chamber?

KILLUS: Not rather than, but that is another criterion, that is, a mechanism that can be used by experts to give reasonable smog chamber simulations is one thing; a mechanism that can be used by experts to give reasonable smog chamber simulations and one that can also be used by novice modelers to give reasonable smog chamber simulations is quite another.

At present, the documentation does not exist for mechanisms to undergo such a test. If you believe that the Carbon Bond mechanism has been adequately documented, in that case, it's the only one, and even then that's only 4 months old. We can't possibly be sure yet.

DIMITRIADES: Somebody suggested earlier that complexity is a factor that varies with the mechanism. The mechanisms that we have now are quite a bit different in terms of number of reactions or complexity. So then, the complexity, that is, the detailed description of the pathways, as well as the set of kinetic data used, are the two elements or aspects of the mechanism which can differ from mechanism to mechanism. My question is then whether it is advisable to use one set of kinetic data for all mechanisms if you just want to evaluate the pathway complexity factor for the various mechanisms?

KILLUS: Do you mean rate constants?

DIMITRIADES: Yes.

KILLUS: For inorganic rate constants, the reactions are pretty similar from mechanism to mechanism. That is very close to the case right now. That is, if you look at the inorganic reaction rate constants for the Carbon Bond mechanism, the Cal Tech mechanism, and so forth, they're almost identical. There may be 5% difference here, 10% difference there, but not a sufficient difference to perturb the mechanisms.

How you go about formulating your organic steps, however, is very different. There is no way to regularize the organic components of mechanisms because they treat different species and different methods of handling the HC's.

The methodology I used to take the Cal Tech mechanism and turn in into sort of a carbon copy of the Carbon Bond mechanism involved a rather complicated analytical procedure that described the organic components of the Cal Tech mechanism in their molecular form to similar sorts of components in the Carbon Bond scheme. That is not something that can be easily done.

JEFFRIES: About half way through my project, I thought about what I was doing and I got really scared. Only half way through. It took me that long to really understand what I'd gotten into.

I had been dealing with Dr. McRae, I had been dealing with Dr. Demerjian, I had been dealing with SAI, I'd been dealing with Dr. Dodge, and there is not very much support for putting somebody else's mechanism up. If you're not careful, you can really get in trouble. We spent a lot of effort just trying to figure out whether we had the mechanism or not. When I talked about the different versions of Carbon Bond, I had different computer print-outs, and as Dr. Killus said, the problem was that it was undergoing all kinds of change. The same thing is true of Dr. McRae's mechanism.

There was only one mechanism I was sure I had and that was Dr. Dodge's. I knew I had hers because I looked at a computer code where it was built in and had been solid for years, and I could pull it out. Everybody else changed everything while I was doing the work.

I will have to differ with Dr. Killus on one point though. Although the manual is out and the mechanism is there, and though it may turn out that Carbon Bond III is identifiable in the same sense that the Dodge mechanism is identifiable, I suspect if you ask him for a copy of Carbon Bond III and you look at one that I've drawn up from this manual, it's not quite the same. Then you get worried about these little fine details of differences. That is because he is still tinkering and playing and whatever. So, I agree that there is a need for documentation or you're going to really get in trouble.

I wouldn't do it over again. It requires too much effort and too much energy to take something that people have sunk a lot of time and effort into, in too many different ways, and to test his system and his system and his system. It's not worth it.

DIMITRIADES: As an afterthought, would you like to have used the same input information, that is, the same assumption for light intensity in the smog chamber, the aldehyde concentrations, etc., and see how the mechanisms would compare with each other?

JEFFRIES: That's not a legitimate test of the mechanism because he made choices when he did his, he made choices when he did his, and he made choices when he did his. And the choices are not independent choices. As soon as you say--

DIMITRIADES: But there's only one light intensity. Of course, I appreciate the problems. I was just wondering whether use of the same input would be desireable just for the purpose of judging the relative performance of the mechanisms, not in an absolute sense, the relative performance. Would that be useful?

JEFFRIES: It's a nonlinear process, and so many factors are important. It may take you 3 months of poring through runs and details and integrated rates to figure out how come in one condition he made more O_3 than someone else did. It's a very complicated process. The first thing you have to know is whether you've got the right mechanism. Just having the right mechanism isn't enough, so the other things you have to know are what light intensity he used, what distribution light intensity he used, and so forth.

BUFALINI: When you compared your original model calculations, you compared the Bureau of Mines chamber data when you tested Dodge?

JEFFRIES: Yes.

BUFALINI: Carbon Bond II, Demerjian?

JEFFRIES: Yes.

BUFALINI: Is there a sufficiently adequate data base from the Riverside smog chamber to test the three or four mechanisms to see whether any one of them would work better?

It seems like when you were comparing those mechanisms some were working satisfactorily at one concentration, and others were working better at some higher or lower concentrations.

I would assume that the newer data that Riverside has obtained have less scatter, but are they sufficient?

JEFFRIES: Each smog chamber has its own kind of uncertainties, and you almost have to know the operator of a smog chamber on a first-name basis. You certainly have to be able to call him on the telephone 25 times a week if you model his runs.

BUFALINI: Okay, that would be my next question then. Is there no end to getting smog chamber data? You're continuing to get some more. I know there is the ERT work that's supposed to be testing EKMA. Are these data going to be satisfactory or what?

JEFFRIES: There has to be a very hand-in-glove cooperation between the guy who's doing the modeling and the model development and the guy who's doing the smog chamber runs.

If I sit down and say, these sets of runs are the ones I'm going to do to test the mechanism, and they're not the ones that are important at all, they don't separate the effects that are in the mechanism--

BUFALINI: So let me get back to what Dr. Dimitriades said. Maybe the whole problem is that he measured his light intensity with his technique, and he measured the aldehydes with his technique, etc. I think the problem with Dr. Dimitriades' data is that the reproducibility is so bad.

JEFFRIES: There were unmeasured parameters. Dr. Dimitriades, at the time he did that, used everything he could get his hands on and he did it the best he could. A lot of things have changed since then.

BUFALINI: Yes, but the new data--

JEFFRIES: That Riverside--

BUFALINI: --they're obtaining are not going to be that good.

JEFFRIES: No, I take it back. That's not quite the same. Is there an existing data base that's adequate for separating mechanisms? The answer to that is no, probably not.

BUFALINI: My next question is--

JEFFRIES: Can you run experiments so that you exercise mechanisms? The answer to that is yes. That's exactly what we're doing. But, you can't necessarily say that because there's a collection of existing data which is adequate for separating out the mechanisms.

MEYER: Is there a list that one could come up with, let's say 8 or 10 different factors that are important in the different mechanisms that one could then check off the list and make sure that their set of experimental data accounted for? Is there a finite number of factors one could consider in designing these experiments to fairly evaluate existing mechanisms?

DIMITRIADES: We know some factors, yes.

JEFFRIES: I didn't say that you couldn't collect together a bunch of smog chamber runs from various conditions and whatever, that a decent mechanism ought to be able to model those to some degree. That is possible.

What happens, though, as you discover when you start doing an application with the new chemistry, is that there is some aspect of the chemistry that needs exercising and the data base you have doesn't exercise that aspect enough. So he calls me up and says, can you run an experiment in which you do this and this and then follow it up with this? And we say okay.

Two weeks later, he gets the numbers back and he now can exercise that piece of the mechanism. It's that kind of operation that's going on. The point is, this work is going on now. I mean, EPA is not sitting here doing nothing. There is a lot of this kind of stuff going on. What happens is--

MEYER: How many different mechanisms would you say are variable?

JEFFRIES: What happens is that I get paid to run experiments; I don't get paid to spend a whole year documenting them and laying them out in beautiful details and making it easy for anybody who wants to use it to do it. It turns out, that's a big effort. You stick your neck out when you do it because what you discover is, your calibration factor was off a little bit on that run back there and somebody's gone off and modeled it. You get into all these kinds of problems.

So, the documentation of both the mechanisms and of the data used is a real hang-up. What happens is a lot of informal arrangements, whereby the work gets done, with few formal operations.

TRIJONIS: First, I would just like to reiterate the comment that Jim Killus made before, that I don't think it's feasible to try to validate the different mechanisms against ambient data, because of the uncertainties in the ambient data.

You don't know if the disagreements are caused by the mechanism or by the meteorology which might not be well known, or by emissions, or what.

I think it might be useful to form a committee or group to select four or five sets of smog chamber data that would be appropriate for validating various EKMA mechanisms. They could choose some Bureau of Mines data, the North Carolina data, the University of Riverside data, whatever. That way the people who are familiar with the data and with the needs of EKMA validation studies could select the data sets they think would be most appropriate for validating EKMA.

Also, in our previous work, we spent a lot of time and effort compiling farily careful stoichial trend data for Los Angeles. I think once we've compiled this it might be a fairly quick and convenient procedure for people examining the alternative mechanisms to just do a validation study using that historical trend data. They could generate a standard isopleth with their mechanism -- I don't know if it's Level I or Level IV, the most simple type of analysis. It would be a fairly simple calculation to use the historical trend data in a routine way for validating or for checking out the various mechanisms, or at least for comparing them, to see which is performing better.

I see at this point two possibilities. We could spend some time deciding what the best smog chamber data to use are. That would probably be the most extensive test. Or, we could do a quick test using some of the historical trend data that we've compiled in our previous studies.

CARTER: What parts of the mechanism should be held constant and what parts--

DIMITRIADES: The reaction pathways?

CARTER: Yes, basically, I mean the parts of the mechanism that should be held constant are the parts that we have the basic laboratory data about, for example, most of the inorganic reactions. But, let's not restrict it to the inorganic reactions.

We know for practically all major HC's, simple HC's anyway, the primary rate constants for decay. And for formaldehyde, it looks like we've got a pretty good handle on its beta rate of--

Maybe the panelists should establish what these things are. Assuming that there is no evidence that something is wrong with the old data, I mean the basic laboratory data, this is what is used in all mechanisms. The modeler should not have the freedom to change or to adjust any known rate constant to fit the data.

DIMITRIADES: That's my concern.

CARTER: --be honest; those are just due to the adjustable parameters. Let's not try to pretend that you're doing something chemical.

It is disturbing in a way, when you're talking about the Dodge mechanism, for example, to identify it with a person. Really, there's only one chemistry that's going on. The problem is that there are a whole bunch of different compounds. Also, not only are there a whole bunch of different compounds, but there are for many of the compounds unknown processes involved in the organic mechanism.

I think the best approach would be to try to validate, try to get a chemically correct mechanism for these individual HC's. Certainly not all 50 million of them, but at least selected representatives of the different kinds of chemistry you have, like alkenes or oxinates, things that are different.

Then, concerning the ambient air data, one could try to look at detailed mechanisms by combining them and seeing how best to represent the complicated mixture by what ratio of the compounds. Or alternately, one could go to lumping schemes that are consistent with basic laboratory data and don't have things like O_3-olefin going to 100% radicals, which we know is not true. We shouldn't have that degree of freedom.

Another problem with this is with the process of studying the individual reactions. They are dynamic and every now and then they'll come across, and all of a sudden another rate constant is known, and that would make somebody's mechanism invalid because he has the wrong rate constant as a meaningful part of it.

In a way I don't like the idea of freezing mechanisms, but I can understand the practical problems. I think the best approach might be to have some sort of ongoing panel that evaluates these things. For example, if some rate constant changes by 10% and it's not critical, they should just stick with the one. But, say the HO_2-plus-NO reaction changes by an order of magnitude or so and it's an important reaction. They shouldn't continue on ahead and use the model which has the wrong rate constant for control strategies. Nobody would really believe you. If you're going to do that, you might as well stick with an engineering approach to start with.

Now, as far as complex HC's, that is, the complex mixes in ambient air, I think it's important to have some idea of what compounds are present in the ambient air so you know how best to try to represent it in your models. Ideally, you would have a detailed model with as many as 30 different compounds and you'd test it against more simplified mixtures using calculations. But, of course, before that's worth bothering with, you need to know what is present in the ambient air.

There is another way to approach it, which is more empirical but maybe more practical. I think these trapped air type smog chamber experiments like Dr. Lloyd was talking about might be fairly useful provided that there are enough control experiments to characterize the chamber effects.

The thing is, with those experiments, you shouldn't just take the isopleths or whatever to be derived from those and apply them directly to the ambient air. You should look carefully at the control experiments and then try to model those results with your model, using the chamber effects that you get from your control experiment, whatever kinds of control experiments you want, like NO_x air radiations. They advocate as a control experiment setting up the only kind that should be appropriate in number and should include that.

But then you can use that to validate your representation of the HC mixture, which then you would apply to the ambient air. With all the problems with ambient air, as mentioned before, it sounds like an impossible task, at least presently, to validate that. Probably, at present, it's a waste of money, really, to spend too much of an effort to try it.

DIMITRIADES: To comment on your last subject, the complexity of the ambient air mixture, in a couple of experiments that were done recently, automobile exhaust was irradiated in a chamber and then synthesized. There was a big difference in results between the real exhaust and synthesized exhaust tests, suggesting that the simulation wasn't correct.

CARTER: Well, there was something you didn't measure that was important.

DIMITRIADES: Right. I guess I would like to invite Alan Lloyd to have CRC consider an experiment, or a study, in which you could put some ambient air mix in a bag, and simulate the air mixture in another, and do such experiments that would either verify or refute whether you can correctly simulate the ambient air mixture based on present knowledge of the ambient air composition.

MEYER: I think one of the single findings that was expressed here today that is of greatest concern is the dependence of this Delta O_3 over Delta HC ratio that one sees with the different mechanisms.

I would like to suggest that some efforts be made to define compositional limits, I guess, within which some of these mechanisms are compared. For example, in the work that we did in St. Louis, we assumed very low aldehyde fractions, simply because that is what the emissions inventory suggested was there. I have a real question as to whether or not some of the findings in that study, particularly considering that some of the mechanisms are apparently very sensitive to the amount of radical initiators at low HC:NO_x ratios, are an artifact of the fact that we selected very low aldehyde compositions for some of the mechanisms that explicitly consider that.

I am wondering if the difference perhaps might not be so great if one were to choose a range of initial aldehyde compositions, let's say, between 5 and 10% of the total NMOC, if that's a realistic range based on atmospheric observations. I'm wondering if one were to do that, whether one would still find this dependence of Delta O_3 over Delta HC on the different mechanisms, or whether a lot less difference occurs.

So, I guess one suggestion I have is that some of the research should be directed toward better characterizing what's out there in the atmosphere so that we can make more reasonable assumptions in some of the smog chamber experiments and in some of the modeling.

JEFFRIES: I didn't show you Level III with the same kinds of slides, the same kind of data. Of course, at Level III we assumed an 8% composition based on Ken Demerjian's input for initial aldehydes. And, of course, the initial aldehyde assumption coupled with two other assumptions going between Level II and Level III cause all Level III simulations to overpredict the O_3. But, they also exhibit quite different Delta O_3 versus Delta HC between mechanisms, days, whatever.

So, the short answer to your question -- changing the aldehydes from 2% to 8% -- is not all there is. You're looking at fundamental treatments of chain links and other factors within the mechanism that are responsible for the slopes, and it's a choice of the assumptions that were made at the time the mechanism was constructed.

KILLUS: I'd like to make a point on this Delta O_3 over Delta HC. As Dr. Jeffries mentioned, in St. Louis the Carbon Bond mechanism seemed to have the largest Delta O_3 per Delta HC, purportedly the great effectiveness of HC control in the EKMA model.

This seemed to be because the Carbon Bond mechanism was somewhat more sensitive to HC's, and, therefore, you get a greater degree of O_3 control. However, that particular thing does not show up in the airshed model. The airshed model is far from predicting the 30 to 40% control of HC that's required for St. Louis. In fact, the airshed model is predicting more like 60% or 65%, 75% total HC.

If you look into it, you discover that probably the reason for this is that in the airshed model there are background HC's. Not a lot, however. In fact, when we were looking through and preparing inputs for St. Louis, we very carefully limited those to fairly small concentrations, about 0.03 to 0.05 ppmC of HC. But, that extra little additional HC is sufficient to give you enough reactivity so that because the Carbon Bond mechanism is more sensitive to the HC's it then gives you more O_3. Well, if you have a greater background reactivity, you have to decrease emissions proportionately to make up for this.

In this particular case, the more complex model wound up giving the same answer as the simplified model, but for different reasons. If you only have one of those effects, in the simplified model or not, you can have an erroneous estimation of the degree of control necessary.

JEFFRIES: I think any modeler who is going to put his name on his mechanism is going to be careful enough to make choices that are pretty reasonable in the beginning. In other words, the driving force for picking out the information in the literature and information that could be most justified, and so forth, it's already there. The problem that we had here was that when we looked around for mechanisms which had been published in the literature and had some potential for being used, we found in existence some mechanisms that effort and work had been put into some time ago but hadn't been worked on since. The Demerjian mechanism hadn't been looked at for about a year or two, ever since he did the Houston work.

There was a mechanism that people knew about. They knew he'd worked on it, they knew he'd published it, and that it would potentially be available. He cooperated by saying, you can have my mechanism. But, he wasn't then going to go through the mechanism and change all the rate constants and make up all the other choices and so forth.

So one of the problems we have to deal with is that we're constantly dealing with evolving, ongoing research projects that are constantly putting out mechanisms. But, that's one thing. Dealing with what a state agency is going to pay a contractor to go find a mechanism and put into his model is another thing.

It's a question that goes back to the documentation issue. Whatever mechanism is documented and made easy to use is going to be the one used.

MARTINEZ: The moment you have several mechanisms, the question has to come up, how do they compare. To speak directly to the question that he raised, I think it is absolutely desireable to have a data base that is used to run all these mechanisms and to compare them against. You cannot compare a mechanism developed on the University of California-Riverside data against a mechanism developed under Bureau of Mines data, using those data. You have to run them on the same data base so you aren't comparing apples and oranges.

You should come up with a standard data base that may be updated periodically, and if you have more than one mechanism, then that data base would be used to compare them.

DIMITRIADES: How far do you go in defining this standard data base? For example, take the University of California-Riverside chamber data and the Bureau of Mines data. The data base includes observed rates or yields as well as light intensities. Should it also include the same kinetic rate constant values?

MARTINEZ: No, I'm talking about the measurements, the experimental data base. Each model will have its own rate constants and kinetics. Like Dr. Jeffries and Dr. Carter say, that varies. But, I'm talking about some chemical knowledge that everybody agrees on.

The moment you get into lumping, whether it's molecular lumping or Carbon Bond lumping, you run into a mine field. The choices are open to reasonable differing assumptions. You don't touch the mechanisms themselves; you just define the data with which they will be run and compared, I think.

JEFFRIES: You make the data easily and readily available, and the guy who produced it has to be available to answer questions about it. He has to make it easy for someone who's developing a mechanism to get hold of the data, put them into his computer, and model them. He has to have a number to call up and say, I did this and this number down here just doesn't make any sense; what do you know about this number?

CARTER: I have another comment. They talk about comparing mechanisms or models. I would think it would be more useful, instead of comparing the different models as a whole, to look at the parts of them. Presumably, if they're all current models, we know the chemistry would be the same in all of them. We should be looking at how they differ and looking at the individual assumptions that are made that differ, for example, the radical source question. Obviously we have different assumptions about that, and other models.

But, that's not the only one. They say in the aromatic mechanism there are different reaction ratios. But just try to break it down to what part the differing assumptions are in.

I think we're getting to the point in our knowledge of the chemistry, not for lumped models, but at least for the molecular models, where the uncertainties are within a manageable number and a great bulk of the parameters are known and fixed.

I think it may be more useful instead of seeing the effect of the isopleth using one whole mechanism, seeing how these mechanisms differ in these 10 or so different ways. We can then do calculations to see the effect of these 10 different parameters and then maybe these in combinations, since obviously there would be synergistic effects.

It's a much more difficult process, but at least that way you may understand what the source of the differences are, which differences are important, and where you need to do the basic research to find out what's causing this.

DODGE: Or determine what smog chamber studies should be run in order to determine if the mechanisms are behaving.

CARTER: Yes, smog chamber studies or basic studies, any sort of study that is sensitive to that particular uncertainty.

JEFFRIES: I agree with that. A part of that is running the models to find out what the model does or doesn't do so you know what to do in the smog chamber and go back and test the model.

DODGE: The models are sensitive to what? Figure out those pieces and then it's very easy to design smog chamber studies that will determine whether or not that mechanism is correct and performing that way.

CARTER: That aspect of the mechanism, yes, that element of it.

DIMITRIADES: In other words, you develop some hypothesis concerning the model performance and then you design the experimental data set to test the hypothesis?

CARTER: Yes. The fact that there is more than one model that reasonably competent modelers are using results in the fact that there are uncertain aspects of the mechanisms that they make different assumptions about.

Just looking at these different aspects, maybe someone would make a different assumption about a radical reaction that's negligible in importance anyway. Then you don't have to bother about that, and the modeler might as well arbitrarily put in something that at least is consistent than something that's an entirely different thing. He should put in something that is sensitive; he should try to identify it.

JEFFRIES: The subtle difference, Dr. Dimitriades, is that you use the model to design the experiment instead of doing the experiment to test the model.

BUFALINI: Is there going to be a consensus of what the sources and the points--

CARTER: Or whether they even exist.

BUFALINI: Obviously this is a problem, because before you start modeling smog chamber data, it seems somebody uses HONO, somebody else uses just an OH source, and others use a combination. There is some talk of perhaps having formaldehyde come off the chamber. That seems like a good starting point--

CARTER: Dr. Dimitriades, as mentioned before, in the last several months or year, a very large proportion of the grants we've been working on are basically aimed at trying to understand this particular problem. This problem is critical to smog chamber experiments, and it may turn out to have relevance outside the smog chambers.

BUFALINI: It's always bothered me that you conveniently put down 8 or 10 ppb of HONO, since the system contained a lot of O_3 the day before when you had used the chamber. It seemed to me that everything should be oxidized very nicely if one used HONO. Similarly, it would bother me if someone were to use a formaldehyde coming off the walls, because formaldehyde would have probably been associated from the previous run, I would assume.

CARTER: Also, you can measure the amount of formaldehyde mix there.

BUFALINI: The problem is you do measure it, though. When you turn the lights on in most of these chambers, unless it's an artifact from the system, if you used atropic acid you will see a little bit of formaldehyde.

CARTER: Well, in our smog chambers, at least now that we've got the technique down to better result, you don't generally see enough to make, certainly not enough to account for the radical source.

Another thing, you mentioned initial HONO. We do have actual direct evidence that initial HONO is present; it seems to be formed heterogeneously in the dark from the NO_x that we put in there. We don't know what the mechanism is.

BUFALINI: This is in the smog chamber?

CARTER: Yes. It seems to be formed in the bulk -- I mean, not homogeneously. But, once you've got the NO_x in, there's a little bit to start with, then if you wait awhile, it goes up. We've measured it directly.

BUFALINI: Yes, but presumably you get HONO even if you don't put NO_x in there originally. If you just put in an inert compound, I mean a paraffin, presumably when you turn the lights on that paraffin will disappear.

CARTER: Yes, but that may not necessarily be HONO; that may be the continuous source. I don't know about that.

DUNKER: I have two comments. One relates to the discussion of documentation of the mechanisms. I think that any mechanism that's being documented should include a test case with all the various inputs so that someone can run this test case on the computer and be sure they've got the right mechanism. I make this comment because recently I was coding up the Carbon Bond II mechanism and I looked at tables in the 1979 and 1980 reports. I just happened to also look at an appendix to Volume II of the 1980 report in which they had a computer output listing, and I discovered five mistakes in the table in reactions which do not balance carbon. In the latest report I got from Gary Whitten, apparently those mistakes have been corrected, so as far as he knows. They do not exist in this latest report dated, I guess, November 1981. But anyone who has coded a Carbon Bond II mechanism from the 1979, 1980 reports, and used Table 36, should be aware that there are five reactions in there where products are missing.

The second comment relates to the sensitivity of mechanisms. I think techniques certainly have been developed recently -- for example, Greg McRae and John Seinfeld have done it for their mechanisms -- where you do a straightforward sensitivity analysis of the mechanism, looking at reaction rates and initial concentrations, and you isolate which reactions have rate constants that strongly affect the species of interest. Those techniques are published in the literature.

CARTER: One other thing about this problem of documentation and validation of the model. What might be useful for control purposes and what the funding agency can do is decree some sort of format for transmitting these things in a computable, readable manner. Then we could, instead of having to go to the trouble of hunting it up in the table, just send off for a computer tape. It wouldn't be that difficult to modify whatever different computer programs we have as long as there was some well known, standard format for transmitting this information. It would save an awful lot of labor.

MARTINEZ: There is not guarantee that computer tape will have any great reactions, anyway.

CARTER: The people who develop the mechanism, as far as their test is concerned would have to put it on the computer tape and use the program that reads it back off again and make sure it's the right one.

DIMITRIADES: Let's switch now to the other subject that is equally important. This is the one related to the complexity of the ambient organic mixture.

I have two questions. One is, is it imperative that we have a smog chamber data set for auto exhaust mixtures or for ambient mixtures, in contrast to synthetic mixtures? Do we need one such data set? We do have one, the Bureau of Mines set. Perhaps we need another more comprehensive, more complete one. But the question is, do we need a set of exhaust or ambient air chamber data?

The other question is, again, one that I have already raised. Suppose we do have mechanisms and models which predict synthetic mixture data very well in small chambers but do not predict exhaust data or ambient air data; then what do we do? Do we continue these efforts to further identify and characterize the ambient mixture in the hope that we have a better understanding of the composition and that we will be able to better simulate those mixtures in the smog chamber? Or, do we want perhaps to tune the model to make the mechanism agree with the smog chamber data on exhaust mixtures or ambient air mixtures?

KILLUS: I can tell you how we handled a similar problem in at least a hypothetical circumstance. Joe Bufalini in the early 1970's, I believe, ran some experiments in which he tried to compare Los Angeles bag samples with some synthetic laboratory mixtures. He observed that the ratio of conversion of NO to NO_2 versus HC decay varied substantially between these two situations. He suggested at the time, in fact, that in Los Angeles air there was a reactive compound that was not measured by their GC column. He hypothesized that this compound was aldehydes.

I went into that and calculated the amount of aldehydes necessary to give that difference in reactivity. It turned out to be only 10% of the carbon mixture, the HC mixture. It's fairly easy for an aged mixture, although this took place at 8:00 a.m., to have in excess of that. The point is, however, that if your emissions mix only has 1% aldehydes, it's very difficult to get up to 10% by 8:00 a.m.. We take that as fairly strong evidence that if there isn't some unknown source of aldehydes in the Los Angeles air, there certainly would be some unknown source of something that's giving an additional reactivity boost to the HC mix. And, we have said that the simplest thing for you to do is just believe that that is aldehydes and add that onto your emissions inventory.

Now, that is concentrating a form of uncertainty in -- quite an assumption -- but it isn't putting it into the mechanism. It is using the mechanism to get at what the source of uncertainty in monitoring is. Perhaps it's not aldehydes. Maybe it's some other HC compound; it may be actually a

radical initiator like HONO. However, you'd need a lot of HONO to boost you that much, and I don't think that's going to increase your NO to NO_2 conversions. But there might be other kinds of oxygenated compounds that could be responsible for that. Whether or not it's aldehydes in this context doesn't necessarily matter. What matters is whether or not it's coming from automobile exhaust, or from an emissions source that you can identify. Also, it's important to know whether or not you have it in your emissions inventory. Even if you can't identify where it is in your emissions inventory, you better have it in the model if you are trying to do an ambient simulation. Otherwise the best mechanism in the world is not going to give you adequate results. Trying to adjust the mechanism to give those better results is lying.

JEFFRIES: In fact, if you didn't know what it was, you'd probably put it in the model as aldehydes anyway.

KILLUS: That's entirely possible, yes.

DIMITRIADES: I think you put the emphasis on a single species like aldehydes or some of the other ones that we are aware of. I would like to suggest, and this is a personal feeling based on work I have done in the past, that we probably deal with the collective effect of several unidentified species. The reason why I think this issue is important is because I doubt that we will ever get to the point of completely characterizing the ambient air mixture. Then what?

LLOYD: I wanted to answer your question of whether we need more smog chamber data. I understood that we've already answered that, but now he's already started it by--

JEFFRIES: He wants to find out whether he wants to take the money back.

DIMITRIADES: No, I don't mean that. I think it's good to have smog chamber data with simple mixtures, but I think it's also good to have data with exhaust mixtures or more real atmosphere-like ambient mixtures. You'll find a big difference between the two types of data, and I think we need to understand why.

LLOYD: The previous question focused on the short-term needs. What can we do now, do we have enough smog chamber data, do we know enough about kinetics to do something?

I was really addressing that. Suppose we make do with this, what should we be doing in the future? I agree with what was said earlier. I also think that your comment is very valid, because what is there as the mix of the HC's change and we see the aromatics increasing? I think it would be very pompous of us to think that we're not going to come up with some surprises. I think we have to have a research program going ahead to look at the character of the atmosphere. So we need some measurements out there, some chamber data, we need some tailpipe emissions testing. But, on the other hand, we do need some synthetic mixes. If we have areas such as Houston, which have different mixtures next to refinery plants, we want to make that applicable. Also, in those research programs, do we want to focus on some of the things that Dick Derwent has mentioned, some of the intermediates, so we can get a better handle on that?

But, that's ahead 5 or 10 years time. We do have some data now. I have worked with Dr. Dodge trying to characterize the kinetics data and the mechanistic data, and those need updating regularly. I think we have some tools to do something with now and we can improve what's going on. Yet, we do need further work. I heartily concur that we need both characterization of the atmosphere and automobile exhaust as well as conducting and refining ongoing tests.

BUFALINI: Dr. Dimitriades, in keeping with your comments earlier about some unidentified something--

DIMITRIADES: Some things.

BUFALINI: Some things, okay. Are we spending the proper amount of effort and funding at the University of North Carolina with this automobile exhaust in trying to identify the oxygenates? As I know, Dr. Jeffries, you're measuring the formaldehyde and I guess some other aldehydes, but are you using the DNPH and the total aldehyde techniques? Are some of the higher aldehydes going to be cross-checked with GC analysis?

I am bringing this up because there is some concern as to whether we're properly identifying the oxygenates. I would hate for EPA to spend this effort in doing the work and then say, maybe we missed some oxygenate that was speeding up the reactions.

JEFFRIES: One of the first things, of course, we want to find out is whether the real automobile exhaust, unaltered, versus the frozen and reconstituted automobile exhaust is the same. If they're not the same, then we've go a lot of work to do to try to figure out why they're not and what's going on. At least we have them all in 200 cc at that point with a factor of 400 enrichment, and we have GC/MS and all kinds of other capabilities to look at. That's a leading question, and we don't know where we're going to go with that yet.

DIMITRIADES: Not the same if you built a dynamometer facility with University of North Carolina money.

JEFFRIES: That's why I'd even want a dynamometer; that's why I want to come out to EPA and use the EPA dynamometer.

BUFALINI: It might be cheaper for you to move your smog chamber out here.

JEFFRIES: No way.

MEYER: I wonder if it would be a useful approach in designing set(s) of test data to first look at the existing types of models for different types of mechanisms that now exist. Perhaps we could come up with some kind of a matrix whereby each of the major mechanisms are listed in the columns of the matrix and then in the rows of the matrix. You could come up with a series of questions about how each mechanism might perform or might be sensitive to these various questions.

Then you could go to the developers of the different mechanisms and try to get the best possible insight into the responses to each of these questions in the rows, to see what the most significant types of questions are likely to be. Then you can go about designing your experiments based on the response of the existing mechanisms.

Hopefully, there wouldn't be too many of these mechanisms, maybe six or eight. That seems to me like a very logical first step to take.

FOLLOW-UP COMMITTEE RECOMMENDATIONS

Richard Derwent, Alan Eschenroeder
Gregory McRae, and Alan Lloyd

The authors of this section of the proceedings attended the workshop and subsequently met as a committee to recommend actions that could be taken by the U.S. Environmental Protection Agency (EPA) to make the best use of information presented at the workshop. This section summarizes and describes the recommendations of the committee.

INTRODUCTION

The Clean Air Act and its subsequent amendments mandate a set of ambient air standards to serve as goals for air quality planning in the United States. The Act establishes a mechanism for improving air quality by controlling primary pollutant emissions. Historically, direct proportionality of pollutant concentrations in air to pollutant emission levels was assumed for designing control measures. Unfortunately, the inherently nonlinear nature of the formation of some pollutants, particularly photochemical oxidants, precludes the use of such simple approaches.

An important characteristic of oxidants is that they are not emitted by pollutant sources, but rather, are formed as products of chemical reactions in the atmosphere. Oxidants such as ozone (O_3), nitrogen dioxide (NO_2), peroxyacetylnitrate (PAN), and hydrogen peroxide (H_2O_2) form in urban atmospheres. These and other pollutants are produced as a result of the action of sunlight on oxides of nitrogen (NO_x) and reactive hydrocarbon (RHC) emissions. Since oxidants are formed by atmospheric reactions rather than emitted in measurable quantities, their control is very difficult. The amount of oxidant formed in any given urban area has a complex dependence on time of day, meteorological conditions, and the nature of the pollutant sources, making the design of effective abatement programs an extremely complex undertaking. Indeed, depending on the initial state of the atmosphere, it is possible to produce an increase, decrease, or no change at all in oxidant levels from a simple strategy based on reducing one of the precursor emissions. These counter-intuitive results highlight the need for a formal methodology capable of predicting the air quality impact of changes in emissions.

Prediction of the effects of emission changes on ambient air quality depends on three basic elements of input data:

- A chemical kinetic mechanism that describes the rates of atmospheric chemical reactions as a function of sunlight intensity and the concentration of the various species present.
- An emission inventory that gives the temporal and spatial distribution of emissions from significant pollutant sources within the airshed.
- A meteorological description, including wind speed and wind direction at each location in the airshed as a function of time, the vertical temperature structure, and radiation intensity.

A detailed formulation of a system linking all these elements is a difficult undertaking because it is necessary to maintain a balance between the input data requirements and the desire for an accurate representation of the underlying physics and chemistry. Partially in response to these conflicting requirements, EPA (referred to as the Agency) has identified four basic approaches that can be used for implementation planning purposes in the United States (Federal Register, 1979):

- Standard EKMA (EPA Level IV)
- City-specific EKMA (EPA Level III)
- Trajectory-specific EKMA (EPA Level II)
- Photochemical dispersion modeling (EPA Level I)

Each of these approaches uses different levels of detail in the treatment of emissions, meteorology, and chemistry. Apart from the Level I analysis, all of the other techniques are based on the Empirical Kinetic Modeling Approach (EKMA).

The EKMA concept involves the use of a chemical mechanistic model to relate O_3 to its precursors, total nonmethane volatile organic compounds (NMVOC) and NO_x. The model and the way it can be used to formulate control strategies are described by Dodge (1977), Whitten et al. (1980), and by Trijonis and Hunsaker (1978). Guidelines for the use of city-specific EKMA were published in March 1981 by the Agency (EPA, 1981). This publication was followed by a further guidance document from the Office of Air Quality Planning and Standards in December 1981. This latter document provided for the use of alternate chemical mechanisms from the standard Dodge mechanism and followed the results of studies that raised questions about the adequacy of the chemical mechanism used in EKMA (Jeffries et al., 1981; Carter et al., 1982). The conclusions that can be drawn from comparisons of EKMA with atmospheric observations are so limited that doubts have been expressed regarding the applicability of EKMA predictions to implementation planning.

This section presents a series of recommendations that offer some guidelines on the valid use of the EKMA concept. To begin, it covers the committee review and perception of the papers presented at the workshop. It also provides some responses to current Agency needs, including proposed actions, using currently available information; identifies research planning goals; and discusses suggested approaches covering a broader spectrum of information but based upon inputs from the workshop. Finally, it outlines a plan of action for the Agency to implement the recommendations.

REVIEWS OF PAPERS PRESENTED AT WORKSHOP

This section contains a brief abstract of each paper presented at the workshop, followed by the committee's comments. The order of the papers follows that of the workshop agenda.

Trend Analysis of Historical Emissions and Air Quality Data (J. Trijonis)

Abstract

Historical precursor trends are documented in Los Angeles and Houston using emission data and ambient data for nonmethane hydrocarbons and oxides of nitrogen. The precursor trends are entered into the standard EKMA model to predict historical ozone trends. The predicted ozone trends are then compared to actual ozone trends to test the EKMA model. The Los Angeles analysis covers the years 1964 to 1978; the Houston analysis covers the years 1974 to 1978.

Review Comments

This study, while simple in concept, is complicated by the large uncertainty in the emission inventory. Although emission-inventory figures for the Los Angeles area were stated to have shown decreases of 29% in RHC and increases of 35% in NO_x, corrections of various inventorying errors over this same time period are at least of this same order; thus, the confidence one can place in this trend analysis is at best questionable. Evidently, the emission trends are smaller than the successive corrections imposed by improvements in methodology. One must, at least, make retrospective corrections in the inventories compiled by the South Coast Air Quality Management District consistent with present knowledge before this difficulty can be overcome.

It is not surprising, therefore, that predicted O_3 levels tended to underestimate observed O_3 levels by as much as 35% for peak hourly O_3 levels at Azusa. The discrepancy is greatly alleviated by the use of the more robust statistic, the 95th-percentile O_3 level. The choice of different statistical measures should be investigated further since it might be feasible to design a more robust criterion for defining compliance with air quality standards. The disagreement seems to be comparable between the case of precursor-derived nonmethane hydrocarbon (NMHC):NO_x ratios and that of emission-derived NMHC:NO_x ratios. Although attempts were made to isolate the emission "footprints" that had most influence on each O_3 monitoring station and to correct O_3 format on for meteorology, no account was made for day-to-day differences in initial chemical composition, mixing-depth composition at the upper boundary, or path differences over the emission pattern. One important conclusion of the Houston study is that the calculated emission changes during the period 1974 to 1978 were not large enough to provide an adequate test of the EKMA model. Despite the limitations that hampered the results of this work, the sensitivity study was a valuable demonstration of the need for an accurate knowledge of the NMHC:NO_x emissions ratio and ambient air quality data. Thus, with improvements in the area noted above, the trend analysis approach can be recommended.

Evaluation of the Empirical Kinetic Modeling Approach As A Predictor of Maximum Ozone (J. Martinez, C. Maxwell, H.S. Javitz, and R. Bawol)

Abstract

The performance of EKMA when used to estimate maximum ozone levels in an

urban area is evaluated. A quantitative measure of EKMA's ability to predict maximum ozone is obtained, and conditions are defined under which ozone estimates for EKMA can achieve specific accuracy levels. The evaluation is conducted using data for St. Louis, Houston, Philadelphia, Los Angeles, and Tulsa. For St. Louis, results are presented comparing EKMA performance using three different chemical models. A Monte Carlo method for using EKMA to predict the distribution of ozone maxima is also described. Applications of the method to the analysis and design of ozone control strategies are discussed.

Comments

This study, on a statistical analysis of EKMA, presents the first results in the treatment of the use of uncertainties in practical decision-making. A central theme to this approach is the probability that the ratio (R) of observed to estimated O_3 lies within the range 0.8 to 1.2. The analysis uses nonmethane organic compounds (NMOC) and NO_x inputs in both standard and city-specific trajectory models to generate the O_3 estimates. The graphical representation of the output is represented as accuracy probability isopleths on the NMOC-NO_x plane. The Carbon Bond II, Demerjian, and Dodge chemical mechanisms are compared.

Qualitatively, all three mechanisms give similar shapes for the over- $(R < 0.8)$ and underprediction $(R > 1.2)$ regions, but the Dodge mechanism is represented best of all of the mechanisms in the $0.8 < R < 1.2$ range. The use of this technique for future conditions could generate O_3 frequency distributions from input joint frequency functions for NMVOC and NO_x.

Another product of this research is the development of a linear transformation from standard EKMA to the city-specific version. This could considerably simplify the generation of working data for air quality planning in specific regions.

The methodology could be improved by extending its use to day-specific meteorological air quality and emission conditions. Worthy of attention is the recommendation that this technique could be employed in a decision-tree analysis for State Implementation Plan (SIP) revisions. Instead of replacing EKMA with more refined approaches, one outcome might be a branch of the tree that combines safety margin concepts with risk assessment. Thus, if O_3 is underpredicted and $P(R < 0.8)$ is low (for a case where O_3 is not greater than 120 ppb) or if O_3 is overpredicted and $P(R > 1.2)$ is low (for a case where O_3 is greater than 120 ppb), the probabilities of falling outside the $0.8 < R < 1.2$ regime can be used with acute response data for O_3 pulmonary effects to generate risk profiles. Then, safety margins on the control strategy can be set by specifying acceptable risks. This is accomplished by running the distribution of output uncertainty from the model around midpoint O_3 levels given by alternative control strategies. A combination of model uncertainty and health effects uncertainty will then generate a profile of risk for each strategy. Backing away from some nominal control point, we can thus get declining risk profiles down to a point of acceptability. To apply the approach of Martinez et al. in this manner, we need to develop a risk module as an added feature.

Predicting Ozone Frequency Distributions from Ozone Isopleth Diagrams and Air Quality Data (H. Jeffries and G. Johnson)

Abstract

Air quality data are used to derive an ozone isopleth surface that predicts the observed frequency distribution, given the observed joint hydrocarbon and oxides of nitrogen distribution. The method uses a seven-parameter mathematical description of ozone isopleth surfaces. The process begins with parameter values that describe the standard Dodge chemistry EKMA surface or a standard Carbon Bond chemistry EKMA surface, and uses a nonlinear convergence technique to find the parameters for a specific city. The method is applied to St. Louis, MO, using Regional Air Pollution Study data, and to Sydney, Australia.

Comments

In addition to the generation of error probability and risk distributions, the uncertainties of EKMA output can be treated by using a broader statistical stratum than the worst hour. Jeffries and Johnson, following the work of Post, have used a technique for curve-fitting the ridgeline region of the EKMA surface to joint distributions of NMOC and NO_x points observed. Reversing the process, they generate an O_3 frequency distribution for precursor input distributions shifted by hypothetical emission control.

As discussed above, both model testing and air quality standard setting, using a reasonable sample of the frequency distribution, produce a more robust result than previous approaches that were restricted to the worst hour of a year. The approach preserves the chemical character of a functional mechanism, fits the observations in the atmosphere, and maximizes predictive success by using an adequate sample of O_3 episodes. Although curve-fitting may be criticized on the basis that it can give erroneous results when applied beyond the range of data, the kinetic adjustments to remove smog chamber artifacts are also nonphysical, as shown by the disparity of results displayed by Jeffries et al. While the approach described in this paper has many desirable attributes, there is one major problem with the analysis. In preparing the frequency distribution, the observed maximum O_3 was not matched with its upwind 6 a.m. to 9 a.m. hydrocarbon (HC):NO_x ratio. The analysis should be repeated to account for the transport affects.

Simplified Trajectory Analysis Approach for Evaluating Ozone Isopleth Plotting Package/Empirical Kinetic Modeling Approach (G. Gipson and E. Meyer)

Back air parcel trajectories are calculated from the site observing the highest hourly ozone concentration in St. Louis and Philadelphia. The EKMA model is then used to simulate the chemistry that occurs within a uniformly mixed parcel of air as the parcel moves along the calculated trajectory. The resulting peak ozone concentration predicted at the site is compared to the actual observed maximum value.

Comments

This work represents a test of EKMA's validity. For Level II analysis, the

Ozone Isopleth Plotting Package (OZIPP) with the Dodge mechanism is applied to 10 days of Regional Air Monitoring Study (RAMS) data from St. Louis. Level III comparisons are made between calculated and observed O_3 levels for St. Louis and Philadelphia. In the Level II test, the authors give the OZIPP-type model detailed input information for an urban environment. This environment has been characterized by data from an extensive research-level network of sensors of air quality and meteorology coupled to a carefully compiled emission inventory. Thus, the Level II test should provide a "best case" situation for success in EKMA applications using the available guidelines and codes.

It was found that the Level II model gave agreement with observations to within 30% for 6 of the 10 days. Four days were significantly underpredicted. Level III gave predictions within 30% for 8 of the 10 days for St. Louis and 23 of the 29 sample days for Philadelphia. These results indicate that the trajectory inaccuracies with the more refined version of the model generate anomalous emissions that degrade its performance. This result illustrates two points: (1) that improvements in the trajectory integration procedures are desirable, and (2) that additional complexity does not guarantee performance enhancement. In fact, it can generate large errors traceable to the complexities breaking down as a result of faulty data. These points also illustrate the value of statistical samples to elucidate performance as opposed to the selection of one worst-case hour or day.

Application of Empirical Kinetic Modeling Approach to the Houston Area (H.M. Walker)

Abstract

Data for the Houston area for the summers of 1977 and 1978 are used to test the EKMA model. Ambient data for ozone, nonmethane hydrocarbon, and oxides of nitrogen are plotted on the standard-EKMA diagram. Predictions by EKMA were found to be variable compared with ambient data. Methods for abstract of high ozone concentrations are discussed.

Comments

Part of the reason for the poor agreement with EKMA predictions is probably the poor quality of the HC data, as stated by Walker. The uncertainty in this aspect of the Houston data here has been recognized for many years. This study also points out the importance of characterizing the improved air quality and the amount of transport of O_3 and its precursors into the Houston area.

Comparison of the Empirical Kinetic Modeling Approach with Air Quality Simulation Models (G. Whitten)

Abstract

A range of models, progressing in complexity from standard EKMA to large grid models, is used to test various parts of the EKMA trajectory model. As a

rule, the physical EKMA model compares closely to the more complex models; the chemical mechanism used can produce the most significant differences between models.

Comments

If the same chemistry, emissions, mixing-layer growth, elevated O_3, and initial conditions are used in two different models, one with a single fully mixed cell, the other averaging over several fully mixed cells (coupled by vertical diffusion), Whitten reports that the results do not differ significantly. Thus, neither the complex chemistry nor the simplified diffusion formulation is a decisive feature in the applications of trajectory models reported here. Whitten derives both the NMOC:NO_x ratio and the initial conditions from emission distributions and realistic flow conditions because linear rollback may not be reliable.

Whitten found that simulations exceeding an interval of one day are sensitive to background pollutant level assumptions. The importance of entraining pollutants other than O_3 from aloft was stressed. The uncertainty imposed by poor guesses of initial conditions can easily be replaced or overwhelmed by the uncertainty introduced by poor guesses of background levels or emission inventories. The same tradeoff is operative in the dilemma of whether to use Lagrangian trajectory models such as EKMA or Eulerian grid models, for example, the Livermore Regional Air Quality (LIRAQ) model.

Deriving Empirical Kinetic Modeling Approach Isopleths from Experimental Data: The Los Angeles Captive-Air Study (D. Grosjean, R. Countess, K. Fung, K. Ganesan, A. Lloyd, and F. Lurmann)

Abstract

A captive-air facility in Los Angeles is described. The use of the results of maximum ozone levels generated in the main and satellite Teflon bags under different hydrocarbon/oxides of nitrogen conditions to test EKMA is discussed. Evaluations of the method for testing different chemical packages in EKMA are presented.

Comments

If the uncertainties in a chemical mechanism can be shown to outweigh considerably those in meteorology and influx rate of pollutants, then a captive-air study, such as the one proposed in this paper, can go a long way toward improving trajectory model accuracy. This kind of experiment has the potential to eliminate the uncertainties of initial conditions, synthetic mixes, and sunlight distribution present in smog chamber laboratory experiments. The complication for this type of experiment is the difficulty in obtaining data on maximum O_3 formation as a function of initial HC and NO_x under the same conditions of sunlight intensity and temperature for which EKMA is used.

If the influx of pollutants and their transport in the air parcel are significant, it is necessary to do an airborne experiment such as that of the

Los Angeles Reactive Pollutant Program (LARPP) of 1971-1975. Surprisingly, none of the trajectory model check calculations makes use of the LARPP data archive. It is based on radar-directed helicopter sampling of air around a radar-tracked array of balloons. Dynamic pollutant profiles in the moving air parcel were obtained for over 30 flights, including 2- to 8-h irradiations. The archive, which is available in documented form from the National Technical Information Service (NTIS), duplicates the conditions hypothesized in EKMA and could be used in conjunction with the captive-air studies.

Description and Comparison of Available Chemical Mechanisms

(G. Whitten and J.P. Killus)

Abstract

The approaches used in several currently available chemical mechanisms are described. Comparisons among the mechanisms are made concerning the following: basic structure, mass conservation, relationship to actual atmospheric species, ease of use with typically available data, verification with either smog chamber or atmospheric data, sensitivity to changes in precursor levels, sensitivity to precursor reactivity changes, and sensitivity to uncertain reactions, rate constants, or parameters.

Comments

Since chemical mechanisms play important roles in EKMA simulations, Whitten and Killus recommend that there should be some validation standard based on the fidelity of representation of the main inorganic and organic functional steps. This paper delineates the content of these steps so that the Agency could derive such a standard for applications to any mechanism that a control agency might wish to employ. Implicit in this approach is the need for adequate documentation on the derivation and application of the chemical mechanisms.

Beyond the inclusion of these basic steps, the standard should encompass such descriptors as the ratio of nitric oxide (NO) reaction to that of HC and the overall rate of NO_x disappearance from the system. Because of the number of mechanisms in use or contemplated for use, this approach would seem preferable to that of listing permissible specific mechanisms. The criteria presented by Whitten could be incorporated in a larger scheme designed to establish rules for performance that must be met for any mechanism employed in the EKMA trajectory model approach.

Effects of Chemistry and Meteorology on Ozone Control Calculations Using Simple Trajectory Models and the Empirical Kinetic Modeling Approach Procedure (H.E. Jeffries, K.G. Sexton, and C.N. Salmi)

Abstract

The effect of substituting different chemical mechanisms in the EKMA model is examined. The four mechanisms examined in the study are: (1) the current EKMA mechanism; (2) the Carbon Bond mechanism used in the Systems Applications, Inc. (SAI) airshed model; (3) the Demerjian mechanism used in the Photochemical

Box Model; and (4) the mechanism developed at the California Institute of Technology. The mechanisms are first evaluated using smog chamber data, and then the predictions of the various mechanisms are compared against data collected in the St. Louis Regional Air Pollution Study program. The choice of mechanisms is found to have a large impact on control-strategy estimates.

Comments

The findings of this report are a major focus of the Agency's concern over the future application of EKMA for regulatory purposes. This work constitutes a reasonable simulation of what well-informed state and district staffs might conclude using various acceptable city-specific EKMA approaches. Four chemical mechanisms were run for 10 Regional Air Pollution Study (RAPS) data days to test an OZIPP-like approach for a city-specific EKMA and for a simplified trajectory model.

A significant statement on the testing of the various chemical mechanisms was that the "experimental uncertainties in the Bureau of Mines (BOM) data base are greater than the differences in predictions among three of the four mechanisms." (The fourth did not fit the BOM results in high NO_x.) In addition to mechanistic uncertainties, large variations in predictability for 6 out of 10 days were also observed in "frozen chemistry carbon monoxide (CO)/HC/NO_x" runs for a set of 30 simple trajectory simulations. Presumably, meteorological or emission inventory inadequacies generate this class of uncertainty.

Probably the greatest cause of concern is the breadth of the uncertainty range in HC control requirements generated by the various models and levels of application. The uncertainties were generated both by differences in the chemical mechanism and by meteorological factors.

Several recommendations are offered in the report. From a practical viewpoint, the suggestions presenting immediate possibility of application are: (1) that planners should be allowed freedom of choices based on technical justification, and (2) that the Agency should provide wind-field methodology improvements in describing trajectories and point sources. Both of these could be provided with available resources; however, increases in latitude of choices will involve Regional EPA staffs in a plethora of quasitechnical discretionary decisions that may require resources beyond those available.

The recommendations in the report lack focus from a research viewpoint in that there is no indication of specific problems or of the need for specific solutions. Whether the suggested further studies will address the key issues is unclear. In other words, since this investigation generates more questions than answers, what is the likelihood that any more physical and chemical research is going to reduce uncertainty? Indeed, the continued use of smog chamber chemical data has revealed experimental artifacts that have not been successfully removed in atmospheric applications to date.

This study revises the proposition that the time may have come for a change from an approach based on a hope that more detail in models generated from more research will improve our ability to simulate observed conditions. Perhaps we should agree that there is a point where uncertainty should be accepted and that some resources should be turned from increasing complexity of models to devising acceptable ways of treating uncertainties in decision-making. Thus, the question of what mechanism or data base should be designated as the best one to use should be de-emphasized, and the question of how to treat the stochastic aspects of the risks incurred using the best combination of inputs should be emphasized. A strength of the Jeffries et al. study lies in its motivation for such a shift in emphasis, because it cannot offer any comprehensive or even diagnostic explanations of limitations of model performance.

Effects of Radical Initiators on Empirical Kinetic Modeling Approach Predictions and Validation (W.P.L. Carter)

Abstract

This study highlights the impact of free-radical precursors, formaldehyde, and nitrous acid on the control requirements predicted by EKMA.

Comments

Carter's paper underscores the importance of representing the role of initial nitrous acid (HONO) and continuous nitrogen dioxide (NO_2)-dependent radical sources in both smog chamber and atmospheric simulations of EKMA chemical mechanisms. Some of the mechanisms proposed for use in EKMA lump these effects into other representations in such a way that causes difficulty in removing chamber artifacts for applications to the ambient atmosphere. The same can be said of the role of aldehydes and their importance in converting from smog chamber to atmospheric characteristics.

Carter emphasizes these points by showing increments of nearly 10% in required HC control for attainment under assumptions of 10 ppb, 5 ppb, and 0 ppb of initial HONO concentration. Up to 8 ppb HONO has been observed in the Los Angeles atmosphere. While this paper illustrates the uncertainties faced by the EKMA user, the likelihood that a control agency can produce long-term reliable statistics on ambient HONO is extremely remote.

RESPONSES TO THE AGENCY'S RESEARCH AND REGULATION PLANNING NEEDS

This section is divided into two parts, one concerned with applying existing methodology and recognizing uncertainty and the other focusing on additional research.

Optional Regulatory Requirements

The actions discussed in the following section are those recommended by the committee using all currently available information.

Determine EKMA Uncertainty Statistics by Tests of the Assumptions and the Results

Evaluation of the performance of air quality models has occupied a significant portion of the recent air pollution literature. The importance of such an evaluation cannot be overstated, particularly in view of the necessity of making control-strategy decisions based on model projections. The essential question underlying all of these studies is how well the model performs when applied to simulate past events. There are three basic steps that need to be undertaken when evaluating the performance of a model:

- Basic assessment of model validity
- Comparison of predictions and observations for particular events
- Analysis of the sensitivity of the predictions to uncertainties in model components

In most previous studies, emphasis has been given to the second step, and discussions of model performance have invariably focused on the inevitable mismatch between predictions and observations. Often it is impossible to ascertain whether the discrepancies result from errors in input data, such as emission inventories, in solution procedures, or in the characterization of the basic physical and chemical processes. While it is important to be able to separate the relative influences of these effects, the practical problems associated with obtaining the necessary information virtually preclude a rigorous and definitive assessment of the formal validity of the overall model using field data. Nevertheless, comparisons of predictions and observations for particular events is a crucial component of the model evaluation.

A Three-Step Process for Evaluating EKMA--

1. A thorough evaluation must be made of each component of the EKMA model, that is, not only of the chemical mechanism but also of the treatment of the meteorological processes. The basic goals of this work should be a dissection of the model components, an analysis of their interactions and, finally, a sensitivity study to determine what features have the most influence on the model predictions.

2. Smog chamber data serve as an essential means for evaluating the performance of different reaction mechanisms. While it is highly desirable to use HC mixtures that replicate those found in urban atmospheres, this approach makes it extremely difficult to determine, in a systematic way, the explanation for differences in predictions. The reason for this difficulty is that, in the case of automobile exhaust or captured-air samples, many of the species present will not be accurately measured or identified. In the face of this dilemma, a dual strategy is required. First, the mechanisms must be compared under conditions for which all the needed composition and irradiation data are available. A number of research groups have assembled information of this form. The testing of each mechanism should involve more than simply looking at concentration-time histories. Every effort should be made to look at the different modes of initiation, radical production, chain lengths, and mass conservation. Once these experiments have been completed and satisfactorily

interpreted, then it makes sense to look at the performance of the mechanisms when they are used to model more complex mixtures such as automobile exhaust. From a careful reading of the report by Jeffries, is is not clear just what the sources of differences in model prediction are.

3. After basic elements of EKMA have been evaluated, the next step is to compare the model predictions against observations. Comparative evaluations of the type described by Gipson and Meyer are greatly needed because these tests expose model weaknesses and, more importantly, the limitations imposed by inadequate data. In these studies all levels of modeling approaches should be tested to determine if the use of more complex techniques improves or degrades the predictions. Note, however, that even though increasing the level of complexity may impose additional data requirements, it also enables the evaluation of more refined control strategies.

In any mathematical-modeling study of real-world situations, thorough attention must be given to the propagation of errors or uncertainties through the model into the prediction of the final outcome. The EKMA modeling study is no different from any other modeling study in this respect. One may reasonably ask how well-characterized the model formulation and input are and, hence how well-determined the prediction is and to what level of confidence. For EKMA, we need to know whether the calculated $\triangle$oxidant/$\triangle$precursor or $\triangle O_3/\triangle HC$ is likely to be predicted with the correct sign, to the correct order of magnitude, or to what 5% to 95% confidence interval. When the reliability of EKMA predictions can be quantified in this way, research attention can then be directed to those areas that contribute greatest to the overall uncertainty.

Uncertainties in model formulation and input span the complete spectrum, from those at the level of computer round-off, to the uncertainties in measured values (whether solar irradiances, emissions, winds, or chemical-rate coefficients that are typically accurate to between ± 10% to ± 100%). Not all uncertainties can be quantified at present, particularly those caused by missing chemistry, excessive averaging over spatial dimensions, and the neglect of particular processes or emission contributions.

Review panels should be established to evaluate the chemical-rate coefficients employed in the models together with their associated uncertainty limits. For some of the more well-studied, fast free-radical reactions, the panel will be able to recommend some atmosphere, 295K-rate coefficients with uncertainties of about ± 5%. However, for the majority of elementary chemical processes thought to be responsible for photochemical smog formation, there are seldom more than two or three studies available, giving sometimes partially conflicting results. Only approximate uncertainty limits can be given under these circumstances, but these are, nevertheless, of some value in the overall assessment of uncertainties.

The treatment of uncertainties in meteorological parameters and emissions is much more problem oriented and will necessarily be more subjective. There is some scope for panel assessments of the uncertainties in motor vehicle emissions, which may be common inputs to many models and study regions.

The next step would be to use the various panel or subjective assessments of uncertainties in a study of model sensitivity to input data. The aim is to evaluate how the uncertainty in input propagates through the model into the predition of $\Delta O_3/\Delta HC$, for example. A variety of techniques may be suitable for this analysis. One is systematic perturbation of one independent variable at a time to evaluate sensitivity derivatives, for example $\Delta O_3/\Delta HC$, where ΔO_3 is a shift in peak hourly O_3 concentration resulting from a perturbation ΔHC in the HC precursor concentration. Another is a random drawing of values (e.g., HC, NO_x, mixing depth, or temperature) from a statistically representative group of ensembles. Each sample is then used to derive a Monte Carlo realization of EKMA-generated O_3 concentration. The compilation of the results gives an expected statistical distribution of O_3 prediction uncertainties.

A second source of uncertainty is generated by artifacts introduced by imperfect mathematical representation of physical or chemical processes. This uncertainty is distinct from that introduced by data errors and can be quantified by relaxing one assumption at a time. This technique does not necessarily require development of completely valid air quality simulation models. Specifically, tests can be conducted by analyzing variance between EKMA output and that of more complex and detailed models. These detailed models can serve as a standard of comparison, but may require too much data to be useful in planning applications. The neglect of vertical variations in species concentration, lateral concentration gradients in plumes, generalization or empirical parameterization of smog chemistry, and the simplification of atmospheric HC reactivity into a small number of surrogate HC's are all assumptions in EKMA models that could be subject to evaluation using the detailed approaches.

Implement Safety Margins that Reflect Prediction Uncertainties

The Agency is faced with a multitude of different model approaches, and sufficient data are not available to pick a single "best" technique. For this reason, the committee recommends a performance-based standard using variable safety margins.

As presently formulated, EKMA-type models show markedly different control requirements with different chemical schemes and other assumptions concerning the fundamental processes involved. It is difficult to appreciate the significance of these differences in predicted control requirements because the accuracy of the individual EKMA model predictions has not yet been determined.

The uncertainty/sensitivity studies proposed in the previous recommendations are aimed toward an evaluation of the probability distribution of the predicted O_3 change for a given amount of HC control; that is, $\triangle O_3/\triangle HC$, for a particular EKMA model. With this probability distribution, it is possible to use statistical confidence testing to decide whether the model predicted $\triangle O_3/\triangle HC$ value is in fact different from zero. Hence, this distribution allows determination of the chances that the reverse outcome may be predicted from the proposed oxidant control strategy.

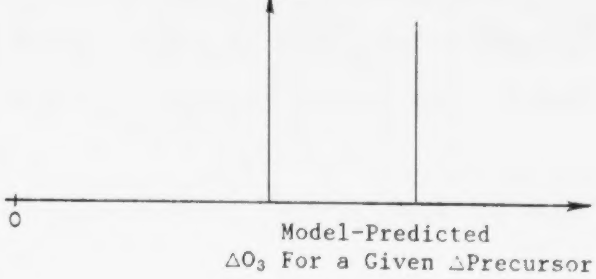
The requirements of the oxidant control measures are to reduce O_3

concentrations to below the air quality standard by control of a particular precursor. This sets a minimum $\triangle O_3$ that must be achieved by the control program. However, accepting that the model output is a probability distribution (see Figure 1) rather than single $\triangle O_3/\triangle HC$ values, it is required that the air quality standard be achieved to a particular statistical confidence level, say to the 1% confidence limit. That is to say, in only 1 chance out of 100, the model predicted outcome would indicate that the air quality standard would not be reached.

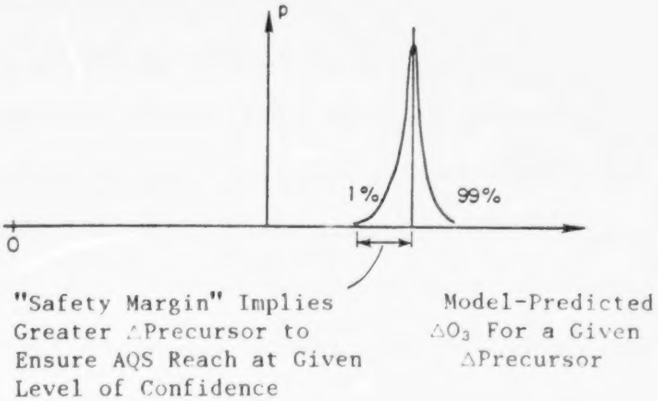
If the model produces a predicted $\triangle O_3/\triangle HC$ probability distribution with a wide probability distribution, then greater $\triangle HC$ values would have to be taken to ensure that the $\triangle O_3$ was adequate to reach the air quality standard within the chosen confidence limit. With a narrow probability density distribution, the amount of extra precursor control required to ensure that the statistical criterion is met would be reduced accordingly. The safety factor required in the precursor control is, therefore, set partially as a basic criterion and partially by the modeling approach adopted. This procedure is constrained by the imposition of some acceptable probability of predicting O_3 levels below those actually experienced in the future. Therefore, all model approaches are equalized with respect to this probability by the selection of appropriate safety margins.

Hopefully, the more detailed models, which require more detailed input, would give tighter probability distributions in their $\triangle O_3/\triangle$precursor predictions and, hence, give reduced safety factors. As an incentive for

CASE 1. Model $\Delta O_3/\Delta$ Precursor Exactly Specified by Input Data


p
0
Model-Predicted
ΔO_3 For a Given ΔPrecursor

CASE 2. Model $\Delta O_3/\Delta$Precursor Exactly Specified by Input Data to "Good Model"


p
1%
99%
0
"Safety Margin" Implies Greater ΔPrecursor to Ensure AQS Reach at Given Level of Confidence
Model-Predicted ΔO_3 For a Given ΔPrecursor

CASE 3. Model $\Delta O_3/\Delta$Precursor Poorly Specified by Input Data to "Poor Model"

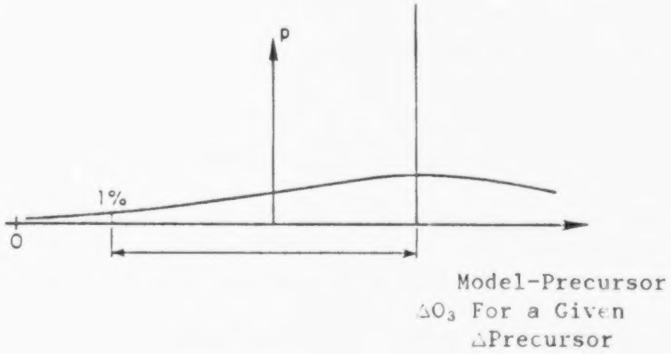

p
1%
0
Model-Precursor ΔO_3 For a Given ΔPrecursor

Figure 1. Model output probability distribution.

improvement, the cost of formulating better models could be set against the advantages coming from the reduced safety factors in control requirements and, thus, against expense in unnecessary precursor controls.

Determine Modeling Time Intervals Needed for EKMA Applications

The time interval prescribed for running a model to generate an EKMA diagram depends on upper-boundary conditions (O_3 and precursors aloft; entrainment or dilution rate), surface boundary conditions (emissions and deposition), initial conditions (species profiles at time zero), and environmental conditions (ultraviolet [UV] insolation rate, temperature, and humidity). From an examination of the various modeling guidelines and, in particular, the paper presented by Gipson and Meyer, a number of possible courses of action is apparent.

Short-Term Approaches--

1. For Level II-type analyses, high priority should be given to improving the recommended procedures for following parcels of air as they traverse the airshed. With relatively little effort, some of the currently available techniques for generating mass consistent wind fields could be extended to provide improved trajectory integration capability.

2. The guideline procedures should be modified to incorporate caveats about the basic validity of a trajectory model when the wind field is subjected

to shear. Ample evidence is available to suggest that one of the major sources of potential error in trajectory model calculations is the neglect of wind shear.

3. Users of EKMA-type procedures need to examine the relative contribution of initial conditions and emissions to the concentration inside the air parcel. Starting the EKMA procedure later in the day or near the center of the city can lead to situations where the influence of initial conditions on O_3 formation is considerably greater than that from emissions. Since it is not clear how the initial conditions might change as emissions are lowered in the future, every effort should be made to minimize the influence of this uncertainty. There are several ways to minimize this influence. One is to run the model long enough so that the effect of initial conditions is no longer seen. Typically, the calculations would have to be performed for a period of time longer than the characteristic ventilation time. Another approach is to start the trajectory well away from any emission source so that "background" conditions might apply. The mass loading into the column is almost entirely derived from emissions as the parcel traverses the airshed.

Develop Statistically Robust Methods of Model Applications

Because of the large risk of error in using a single rare event as a basis of air quality planning, ambient standard setting is moving toward the use of samples of data days to represent episodes. Thus, applying models to groupings of data in the same manner becomes desirable.

The straightforward application of this principle is to select a standard sample of days (say, the top fifth-percentile stratum of the peak O_3 events) and apply the model to each day with the various strategies. Statistics would be generated for future air quality predictions driven by the same meteorological variability as that of the set of design days. Another approach would be to draw randomly a subset of the sample; however, care must be taken to avoid serious truncation errors.

The significance of truncation errors can be tested by selecting successive batches of model runs beginning with a relatively large sample of cases. Each successive batch is either a randomly drawn subset of the last or a stratum of the last batch rank ordered by peak O_3 level. The spread of uncertainty resulting from these several truncations will provide a numerical experimental result for general use in assessing uncertainties in future routing calculations of O_3 control strategies.

The basic goal of this work should be to assess if the current or proposed day selection procedures result in a set of reliable conditions for modeling studies. For example, the day that has the worst air quality may require a lower level of precursor control under some other meteorological conditions.

Finally, if the sample called for under a robust standard is too large for either of the above approaches to be practical, a Monte Carlo technique could be applied. The repeated model runs would be driven by meteorological conditions drawn from the entire sample space required by the standard. This method is clearly less desirable than an actual representative subset of days, but it will out perform single calculations of mean or external conditions from the criterion of robustness.

Develop Computer-Aided, Remotely Accessible, User-Interactive Techniques for EKMA or EKMA-Like Models

One way of maintaining quality assurance of SIP modeling work done by state and local agencies is to centralize the computer codes. The agencies can gain access to the code library through remote terminals using an extension of the UNAMAP system or a new stand-alone system. User-friendly software would be implemented to minimize resistance of personnel unfamiliar with modeling approaches.

Because of the growing number of choices that must be made in O_3 SIP modeling, fashioning a workable set of technical guidelines that are understandable to agency users is a difficult task. A key aspect of the interactive system would be a need to supply the program with uncertainty estimates to generate sensitivity results. Default values could be provided for users who are unable to input error statistics.

Terminal and communications hardware would be standardized to fit the budgets and needs of a typical user agency. The Agency would maintain assistance through the annual workshops recommended below and through publications documenting updating of the codes and, possibly, of a standardized data base that might be archived centrally.

Research Planning Goals

In addition to the previous programs, the Agency should identify and implement programs of a longer-term nature to acquire the data necessary to improve EKMA methodology. The following areas are recommended for additional study.

Identify Additional Criteria for Guiding Evaluation Protocols

The comparison of model calculations for selected trace-gas species with the recorded atmospheric observations is the only available means of assessing the reliability of the models. These comparisons are necessarily limited by the spatial averaging inherent in the model formulations and by uncertainties in the ambient concentration data base resulting from instrumental imperfections or inadequate siting of the instruments. These comparisons are subjective, and what may pass for good agreement may be fortuitous with inadequate models and an imperfect ambient data base. Furthermore, reconciling good agreement in one part of the model with poor agreement elsewhere can be difficult when the atmosphere, and hence the models, are meant to be interactive.

To go further and evaluate the model's representation of the outcome of changing precursor emissions on predicted O_3 concentrations is to place further emphasis on the comparisons between models and observations. Whether the statements from the models about the possible decrease of O_3 concentrations following precursor emission controls realistically describe what will actually occur in the atmosphere depends on their accuracy and coverage of all relevant processes.

Model evaluation will require a detailed treatment of model sensitivity to uncertainties in input data, the removal of the subjective elements of model comparison with observations, and the identification of critical criteria for the evaluation of model performance. Broadly, we could envisage the following framework (Figure 2) in which sensitivity/uncertainty is linked with model comparison through the probability density distribution of the predicted ΔO_3:Δprecursor ratio.

For each chosen value of the input parameter within its uncertainty distribution, a given value of the evaluation criterion is predicted in the standard atmosphere together with a ΔO_3:Δprecursor ratio found from an additional model run with reduced precursor emissions. As the input parameters are varied throughout their accessible ranges, the probability distributions of the evaluation criteria and the ΔO_3:Δprecursor ratios are plotted out. However, some of the combinations of input parameters should lead to the prediction of unphysical values for some of the evaluation criteria and, hence, the corresponding ΔO_3:Δprecursor ratios should accordingly be deleted. The better the atmospheric determination of the evaluation criteria and the more sensitive the model is to this parameter, the more unreal simulations can be eliminated from the ΔO_3:Δprecursor distribution. A model comparison becomes a model validation when it restricts the probability distribution of the predicted outcome.

Hopefully, the more complicated models, with their better representation of the atmosphere, would be capable of better performance. That is, the more complete models would be more readily checked against the atmosphere, so that the range of valid ΔO_3:Δprecursor ratios would be much reduced. The tighter the probability distribution of the ΔO_3:Δprecursor ratios, the less the safety factor required in the precursor controls.

This model evaluation requires the identification of suitable performance criteria. These criteria are parameters that are amenable to theoretical investigation and readily measured in field studies. Species concentrations are obvious evaluation criteria, but there are also many others that come to mind. Certain diurnal variations in species concentrations, midweek-weekend difference, O_3 versus temperature correlations, or ratios of species concentrations may also be suitable for this purpose.

To check all aspects of model performance, attention to species other than O_3 itself is warranted. Model evaluation may well require additional observations of precursors, other photochemically generated secondary pollutants, free-radical species, temporary reservoir species, photochemical degradation and product species, and unreactive species to check emission and dispersion. In this respect, species such as PAN, hydroxyl radicals, N_2O_5, nitric acid (HNO_3), H_2O_2, and sulfate aerosol require investigation or further

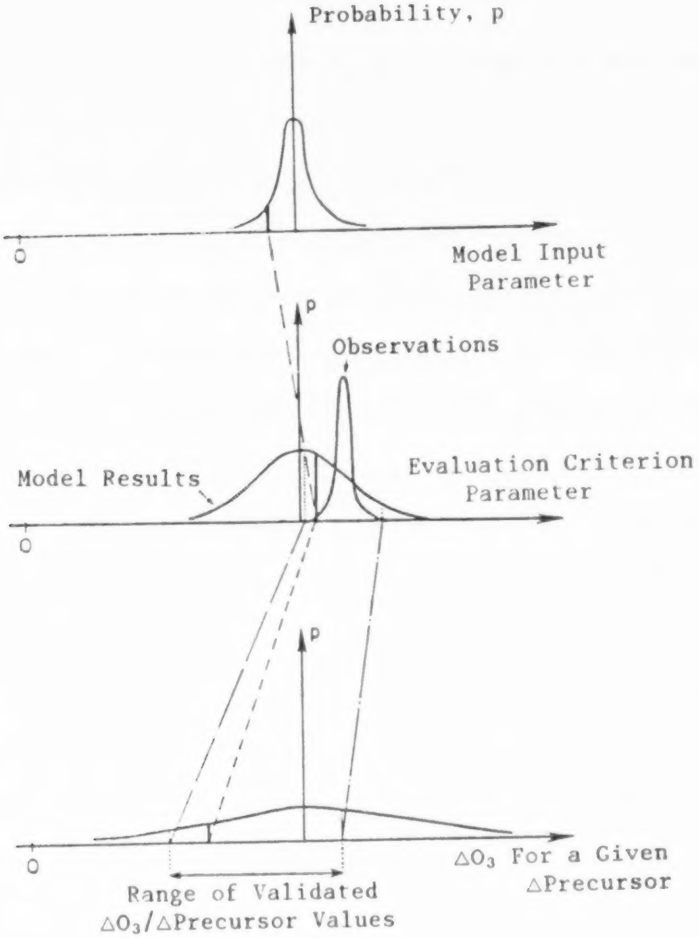

Probability, p
0
Model Input Parameter
p
Observations
Model Results
Evaluation Criterion Parameter
0
p
0
ΔO_3 For a Given ΔPrecursor
Range of Validated $\Delta O_3/\Delta$Precursor Values

Figure 2. Framework in which sensitivity/uncertainty is linked with model comparison through the probability density distribution of the predicted ΔO_3:Δprecursor ratio.

monitoring to test model representations of the underlying atmospheric physics and chemistry.

Investigate the Possible Application of EKMA to Pollutants Other Than Ozone

Background -- Currently, the EKMA model is used for calculating the maximum O_3 concentrations predicted from the initial mix of nonmethane hydrocarbons (NMHC) and NO_x under defined meteorological conditions and sunlight intensity. However, the model also calculates the concentrations of product species other than O_3. Nitrogen dioxide, PAN, and HNO_3, for example, play key roles in influencing the maximum O_3 predicted by the chemical model. It is possible, therefore, that EKMA could also be used for NO_2, PAN, and gas-phase HNO_3. The maximum short-term concentrations of these species as a function of initial HC's and NO_x could be calculated. If sulfur dioxide (SO_2) is included in the chemical mechanism, then the production of sulfate by gas-phase processes, particularly oxidation by the hydroxyl radical, can also be predicted as a function of HC's and NO_x. Note that the prediction of HNO_3 will be a maximum value since it does not take into account any reaction with ammonia (NH_4) to give ammonium nitrate (NH_4NO_3).

Suggested Approach -- The EKMA approach for species other than O_3 has already been explored by several workers (Whitten et al., 1980; Lloyd et al., 1982). The approach appears to have merit for further study, and possible applications of the approach to NO_2, PAN, HNO_3, and sulfate should be explored. Some comparisons for NO_2 may be made with predictions from other commonly used models with simple chemistries to compare the predicted values with both approaches. Using EKMA for the prediction of NO_2 permits the incorporation of realistic chemistry for the oxidation of NO in a relatively simple model.

Identify Critical Measurements of Ambient Volatile Organic Compound Composition Based on the Current Chemical Kinetic Modeling and Environmental Chamber Needs

Background -- Standard EKMA partitions the NMHC into two components, propylene and n-butane. This choice was made on the basis of the chemical model developed by Dodge; the proportion of propylene to n-butane was derived by obtaining the best fits between computed and measured O_3 from the BOM smog chamber studies (Dimitriades, 1972). The BOM studies were carried out with automobile exhaust representative of the early 1970's. However, significant changes in automobile emission controls and in gasoline composition have occurred since the studies. There is also some question about the representativeness of pure automobile exhaust for urban areas, which may have a significant component of stationary-source volatile organic compounds (VOC).

Identifying the key VOC compounds and their relative proportions in the ambient atmosphere of the major urban areas in the United States is important for two reasons:

- To ensure that the chemical mechanism derived adequately treats the chemical transformations of the major species. For example, with the increasing aromatic HC content in gasoline and in urban atmospheres, it is important that the chemical mechanism adequately treats the photooxidation of these species.

- To design smog chamber experiments to test and define EKMA for current

> and future uses, it is important to identify the specific compounds in the atmosphere so that reasonable simulations with this mix may be carried out. Results of these experiments can then be compared with those of experiments carried out with pure auto exhaust.

Clearly, chemical mechanisms and smog chamber experiments should keep pace and be consistent with the changing urban mix, for example, increase in aromatic content and use of alcohol fuels. A design strategy based on a mix obtained in previous years may not be as effective in reducing O_3 when the future mix of HC's changes.

Suggested Action -- Detailed HC data should be collected at the key urban areas in the United States that have not attained the O_3 standard. Diurnal analyses of ambient HC's should be carried out during the season exhibiting peak O_3 concentrations in the major nonattainment urban areas. These data should be archived and regularly updated (every 2 to 3 years) to keep pace with possible changes in the mix.

Oxygenate concentrations are important inputs to the EKMA model. Therefore, the ambient analysis should also include oxygenated HC data. Specifically, formaldehyde and some of the higher aldehydes and ketones should be measured at the same time as the NMHC.

COMMITTEE RECOMMENDATIONS BASED ON WORKSHOP INPUTS

This section of the committee report contains the committee's recommendations, which are based on information provided formally or during discussions at the workshop, but which are not necessarily in response to the Agency's specific requests.

Development of Design Standards for Air Quality Control Strategies

The Empirical Kinetic Modeling Approach is a tool used in the development of an air quality control strategy to assess the amount of emission reduction necessary to bring the air quality of a particular region into compliance with the air quality standard for O_3. However, design of an air quality control strategy is a highly complex process, and the committee feels that a new approach should be examined involving separate air quality control criteria and design documents.

An air quality control planning methodology document for photochemical pollutant strategies would make use of the information provided already in criteria and control technology documents. It would provide methods and procedures based on our scientific and technical knowledge for designing air quality control strategies. Practical alternatives would be offered to local and regional control agencies, and criteria for selecting appropriate approaches would be spelled out in terms of resources at the disposal of the particular agency (e.g., personnel, data, hardware, and software). This information would include a review of O_3-formation, process, control-option availability, availability of data on emissions, air quality and precursors, estimates of uncertainties in each of these areas, and an assessment of methods to relate emissions to air quality based on the reviewed data availability. This work should also include a study of the methodologies and problems encountered in the design of control strategies prepared as part of the SIP process. State and local agencies should be canvassed to document their views and comments on the planning processes.

This task should be performed in a thorough and unbiased way. The National Academy of Sciences would appear to be one appropriate vehicle to meet these goals.

Based upon the information in the planning methodology document, a set of detailed procedures should be developed and set forth in a control design document. This document would update existing guidance documents and would explicitly provide a set of steps to be followed by control agencies in planning for O_3-standard attainment. This design document would be similar to the guidance provided in the Federal Register for control officials to apply to various levels of EKMA analysis. Thus, the required input data for emissions with specified temporal and spatial resolution, the air quality concentrations for initial conditions of O_3 precursors, key intermediates and O_3 background and transport, the meteorological data requisites, and uncertainty bear on all the input data.

The next phase of the program would be to review the results of the above procedure. This review should include an assessment of the success of the various individual procedures and of the final result. The overall plan would permit the Agency to revise and update the criteria and design documents.

The committee feels that the program outlined above represents a significant attempt to formalize some current procedures and to provide constant feedback from the generation of improved basic data to the translation in the control implementation arena. This link needs substantial improvement over the current methodology.

Information to Be Supplied From a Research Program

The information required from research planning goals is discussed briefly above. Some additional research areas and data requirements needed from research programs to improve the current quality of data for the implementation of regional-specific EKMA are discussed below. Table 1 summarizes the variety of topics (some of which were discussed at the workshop) meriting additional research.

Two additional topics that offer considerable scope for future research are: the incorporation of particulate formation processes and a study of currently unregulated pollutants. Technically, the most challenging is the implementation of the aerosol mechanics. The capability to predict the formation and growth of fine particulates will be an integral element of any strategy directed at improving visibility in urban areas.

In addition to the species of regulatory interest, most air quality models also predict the concentration of many other pollutants that have known or anticipated effects on health and welfare. For example, gas-phase HNO_3 can

TABLE 1. SUMMARY OF AREAS AND QUESTIONS FOR ADDITIONAL RESEARCH

Turbulence

Entrainment Process at Inversion Base
Diffusive Transport Under Stable Condition
Cost-Effective Closure Models

Objective Analysis Procedures

Wind-Field Generation in Remote Areas
Applications of Remote Sensing
A Priori Generation of Mixing Heights

Surface Removal Processes

Characterization of Deposition for Different Stabilities
Surface Affinity Characterization

Point-Source Treatment

Dispersion Coefficients
Procedures for Imbedding Plumes in Grid Model
Plume Rise Calculations in Arbitrarily Stratified Environments

Chemistry

Improved Representation of Aromatic HC Kinetics and Mechanisms
Temperature Effects on O_3 Formation
Reactions Involving Natural HC Emissons

react with NH_3 to form particulate NH_4NO_3, that in turn can have a major influence on visibility degradation. One area that deserves special attention is the feasibility of preferentially abating some of these pollutants as part of ongoing oxidant and particulate control programs.

In many areas, further model development is hampered more by the paucity of measurements than by a lack of understanding of the basic physics and chemistry. Data deficiencies occur in three areas: field measurements needed to verify a chemically resolved model, source test information required for construction of emission inventories, and experimental determination of basic chemical data. These requirements are detailed in Tables 2 and 3. While not strictly a part of a measurement program, one aspect that is often ignored is a thorough assessment of the accuracy of the basic data. This consideration is particularly relevant to the emission information. Unless the emission data have been prepared at a level consistent with the desired accuracy of the model predictions, there is little point in using air quality models. Consistency checks need to be applied to individual sources, source classes, and the region as a whole, and thus should include: fuel-usage patterns, operating conditions, pollutant ratios, exhaust composition, and control efficiencies. One useful approach is to compare the results from top-down and bottom-up estimating procedures. These methods can provide bounds on the accuracy of emission inventories. A formal methodology using weighted sensitivity analysis techniques is described by Ditto et al. (1976). Recently, McRae and Seinfeld (1982) have estimated the error

TABLE 2. SUMMARY OF METEOROLOGICAL MEASUREMENTS NEEDED FOR MODEL EVALUATION

Wind Measurments

Vertical Shear Distributions
Flow Patterns Close to Mountains (Upslope Flows)
Magnitudes of Nocturnal Drainage Flows
Quantitative Evaluation of Monitoring Site Exposure
Characterization of the Effects of Surface Roughness

Mixing-Height Distribution

Increased Spatial and Temporal Resolution of Mixing Height
Effect of Mixing-Height Distributions Close to Mountains

Solar Radiation

Detailed Spatial and Temporal Measurments of UV Flux

TABLE 3. SUMMARY OF NEEDED CHEMICAL MEASUREMENTS

Concentration Measurements--General Aspects

Quantitative Evaluation of Inteference Effects
Detailed Characterization of Monitoring Site Exposure
Establishment of Bounds on Measurements Resulting from Errors and Averaging
Improved Resolution of Vertical Concentration Distributions
Routine Measurements of Certain Noncriteria Pollutants

HC Measurements

Spatial and Temporal Variations of HC Reactivities
Characterization of Aldehydes and Natural HC's
Need for Increased Species Resolution Beyond Total Hydrocarbon-Reactive Hydrocarbon-Methane (THC-RHC-CH_4)

Background Air Quality

Values away from Urban Region
Vertical Profiles of O_3
HC Concentration and Composition
Concentration of NO, NO_2, and O_3

Source Profiles and Emission Factors

Detailed Emission Distributions from Mobile Sources
Chemical Composition and Solvent Use by Industries
Extent and Magnitude of Emissions from Gasoline Evaporation
Industrial Fuel-Usage Patterns
Improved Characterization of Emissions from Area Sources

bounds on emission inventories as part of an overall model performance evaluation. Uncertainties in mass emission rates and chemical reactivity are included. This method could be widely applied in future studies.

Short-Term Recommendations

Based on the results of a systematic sensitivity analysis of the EKMA model concept, as well as some alternative approaches, research priorities should be established for the items raised in Tables 2 and 3.

AN ACTION PLAN FOR THE AGENCY

The papers given at the workshop and the recommendations of the panel both point to certain active steps that the Agency can follow to (1) resolve the dilemma posed by EKMA uncertainties and (2) meet deadlines only a few years away for updating SIP's.

Even with unlimited resources, it is doubtful that a single well-supported technical approach could be evolved for O_3 control strategy planning under the existing constraints. What then is the best course of action for the Agency? Following our short-term approaches, it will be necessary to make do with available techniques, but also to translate an enhanced understanding of their limitations into a practical policy guiding user agencies. The action items enumerated below are steps over and above a research program needed to satisfy the regulatory mandates placed on the Agency.

Assessment of the Present Status

Several of the efforts described were in partial stages of completion as reported at the December 1981 workshop. The Agency should first undertake an objective critical review of where the work stands now and what the prospects are for completing any unfinished tasks. Some of the yardsticks against which the current work can be measured are found in this report. Of special interest will be the results of EKMA performance statistical evaluations (both brute force and Monte Carlo) and the data from vehicle exhaust smog chamber runs. Careful interpretations of these research outputs placed on the backdrop of the workshop information will set the stage for the remaining action items in this plan.

Review of Recently Submitted SIP Updates

An update cycle for SIP's has just been completed. Whatever has been used in these SIP's for O_3 control strategy planning will give the Agency a clear idea of the level of skill, the quality of data, and the facility with model applications presented by state, regional, and local air quality agency staffs. The progress made beyond the previous round of SIP submittals will help establish requirements to be placed on methodology improvement that are consistent with expected learning curves of users. An important part of SIP review will be an evaluation of (1) the extent to which results of earlier SIP estimates have been observed in air qualty improvements, and (2) the revision of needed reduction in HC's and NO_x resulting both from inventory corrections and model changes.

Establishment of a Heirarchy of Approaches

Following the spirit of the multi-level scheme originally proposed for EKMA, a set of alternative approaches should be formulated based on the findings of the two action items discussed above. Various forms of EKMA may or may not be included in this heirarchy. For each approach the statistics of uncertainty should be assigned, based, wherever possible, on technically defensible sensitivity test data. These statistics can be expressed as probability of error for each method and for each class of input data. Implicit in this action item is the development of a capability for discriminating causes of error and for classifying input data sets within prescribed quality categories. Each alternative within the heirarchy will have clean and objective ground rules, which govern the assignment of uncertainty statistics.

Assignment of Acceptability Scores of Various Levels of Uncertainty

Corresponding to each distribution of errors from the methodologies will be an expectation of some potential for harm as a result of underestimating peak O_3 levels achieved with a given control strategy. (Conversely, errors in the other direction generate probabilities of needless social costs incurred for overly stringent emission-reduction requirements.) Errors of the first kind should be scored using values based on health risks so that a quantitative assessment of safety margin can be assigned to each of the alternative approaches.

Probability of exceedance of some ambient standard or number of persons exposed to levels violating this standard both fall short of being continuous measures of acceptability. The error penalties or margins of safety to be assessed to each control agency will, therefore, be set so that each planning technique for O_3 prediction results in the same acceptability index expressed in terms of probability of some adverse effect. Thus, the methods and data sets that merit relatively high confidence levels will be penalized less than cruder approaches to afford the same degree of protection. A cost-benefit module can be added to the product of this action item directly if that becomes part of Agency policy needs.

Development of Reviews and Documents

The panel findings recommend the formation of a review group and the production of certain documents. The Agency could enhance the objective formulation of goals and selection of techniques by setting up peer-review mechanisms that formalize some of the evaluations and permit outside feedback to the Agency. The review group could get comments from the public, industry, and other government agencies on the proposals generated under the above action times. It will then set up a framework for the documents dealing with background information as well as design standards for control strategy. Focused effort on each document could be handled by a third party like the National Academy of Sciences, which already has provided EPA support on the background for criteria documents and the examination of special topics.

Promulgation of Regulations

The background and technical policy built up in the previous action items will provide a firm foundation for regulatory requirements for the preparation of O_3-attainment SIP's. The regulations themselves could be relatively simple and incorporate by reference the outputs of the above action items. Support provided by an active review system and explicit documentation that will have preceded the rulemaking itself will streamline the process considerably.

Each of the steps enumerated above embodies implicitly the scientific recommendations given elsewhere in the report. This action plan is offered as a set of tasks that will build on the present store of reseach information over a 2- or 3-year period. Simultaneously, it is assumed that ongoing research will be building a basis for the next cycle of planning methods improvement. Attainment of perfection of chemical mechanisms and atmospheric models is not clearly as important here as learning to make decisions in a world of uncertainty. The sequence of steps traced above, therefore, leads more toward the goal of reasonable applicaton of imperfect methods than toward one of complete understanding of chemical or physical processes.

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